ISOTOPES AND RADIATION TECHNOLOGY

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION / DIVISION OF ISOTOPES DEVELOPMENT, UNITED STATES ATOMIC ENERGY COMMISSION, by P. S. BAKER, A. F. RUPP, and ASSOCIATES, OAK RIDGE NATIONAL LABORATORY

Spring 1966

● VOLUME 3

● NUMBER 3

TECHNICAL PROGRESS REVIEWS

To meet the needs of industry for concise summaries of current atomic developments, the Atomic Energy Commission is publishing this series, Technical Progress Reviews. Issued quarterly, each of the reviews digests and evaluates the latest findings in a specific area of nuclear technology and science.

The five journals published in this series are:

Isotopes and Radiation Technology P. S. Baker, A. F. Rupp, and associates
Oak Ridge National Laboratory

Nuclear Safety Wm. B. Cottrell, W. H. Jordan, and associates
Oak Ridge National Laboratory

Power Reactor Technology
Argonne National Laboratory

Reactor Fuel Processing Stephen Lawroski and associates
Chemical Engineering Division, Argonne National Laboratory

Reactor Materials R. W. Dayton, E. M. Simons, and associates
Battelle Memorial Institute

See the back cover for availability information.

The views expressed in this publication do not necessarily represent those of the United States Atomic Energy Commission, its divisions or offices, or of any Commission advisory committee or contractor.

Availability of Reports Cited in This Review

Unclassified AEC reports are available for inspection at AEC depository libraries and are sold by the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Some of the reports cited are not available owing to their preliminary nature; however, the information contained in them will eventually be made available in formal progress or topical reports.

Unclassified reports issued by other Government agencies or private organizations should be requested from the originator.

Unclassified British and Canadian reports may be inspected at AEC depository libraries. British reports are sold by the British Information Service, 45 Rockefeller Plaza, New York, N. Y.; Canadian reports (AECL series) are sold by the Scientific Document Distribution Office, Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

Classified U. S. and foreign reports identified in this journal as Classified may be purchased by properly cleared Access Permit Holders from the Division of Technical Information Extension, U. S. Atomic Energy Commission, P. O. Box 1001, Oak Ridge, Tenn., 37830. Such reports may be inspected at classified AEC depository libraries.

Contents

Isotopes and Radiation Technology

Vol. 3, No. 3

I General Review 179
Isotopes Information Center at ORNL 179
Scope 179
Input 180
Indexing, Storage, and Retrieval 181
Output 181
Personnel 181
How To Contact 184
Your Help 184
Publications by Isotopes Information Center 184
New Developments and Trends in the Isotope Industry 185
Growth Statistics 185
Future Trends 188
Conclusion 191
References 191

II Isotope Production and Development 193
The Chemistry of Electromagnetically Separated Stable Isotopes . . . 193
General Considerations 193
Product Purification 194
Analysis 195
Product Purification Methods 196
Photochemical Separation of Isotopes 200
Mercury 201
Lithium 202
Chlorine 203
Uranium 203
Hydrogen 203
References 203

III Isotope Technology Development 206
Preparation, Properties, and Uses of Kryptonates in Chemical Analyses 206
Preparation and Properties of the Kryptonates 207
Applications of the Kryptonates in Chemical Analyses 210
Radioisotope Instruments in Industry and Geophysics 214
The AEC Program in Radioisotope Instrumentation 214
Summary of the Symposium on Radioisotope Instruments in Industry and Geophysics 217
References 228

IV Food Irradiation 232
Radiation Sensitizers in the Preservation or Sterilization of Food, Drugs, and Medical Supplies 232
Radiation Sensitization of Bacteria by Chemicals 232
Conclusions 234
References 234

V Process Radiation Development 236
Irradiated Wood–Polymer Combinations 236
The Effect of Radiation on Cellulose 237
Graft Copolymerization with Cellulose 238
Wood–Plastic Combinations 238
Conclusions 242
References 243

VI Applications in Medicine 245
Tracer Theory: A Review 245
1. Basic Concepts 245
2. Formulation of a Problem 246
3. Physical Dimensions 246
4. Brief Historical Review 247
5. The LFCA Method 249
6. Examples 251
7. On the Physical Significance of LFCA 253
8. Other Forms of Tracer Analysis 254
9. Concluding Remarks 256
Appendix: Definitions of Some Common Concepts 257
References 260

VII Isotopes Around the World 263
Radioisotope Programs in Euratom 263
Bureau Eurisotop 263
Labeled Compounds 266
Radioisotopes in Yugoslavia 267
Reactor Production of Radioisotopes; Labeled Compounds . . . 267
Cyclotron Production of Radioisotopes; Labeled Compounds . . 268
Use of Radioisotopes in Veterinary Medicine 269
Third Symposium on Use of Radioisotopes and Radiation in Industry 270
Radioisotopes in Australia 270
Use of Sources 271
Use of Tracers 272
Importation of Radioisotopes into West Germany 273
Availability of Stable Isotopes in East Germany 273
References 275

VIII Miscellaneous Items of Interest 280

Issued quarterly by the U. S. Atomic Energy Commission. Use of funds for printing this publication approved by the Director of the Bureau of the Budget on December 23, 1965.

Isotopes and Radiation Technology is a Technical Progress Review prepared by the Isotopes Development Center, Oak Ridge National Laboratory, at the request of the Divisions of Technical Information and Isotopes Development, U. S. Atomic Energy Commission. This Review is intended to assist those interested in keeping abreast of significant developments in the fields of isotopes and radiation technology. It is not a comprehensive review of all literature published in this field during a given quarter; rather, it is a mechanism for presenting concise, selected reviews of information on subjects of prevailing Commission interest as it becomes available.

This Review attempts to relate the published results of research and development sponsored by the Division of Isotopes Development to significant developments in radioisotopes and radiation technology, as reported in the world literature. Coverage includes isotope production and development, isotope technology development, isotope applications technology, process radiation development, and radiation processing of food and medical supplies.

In addition to reviews of current literature and special review articles dealing with specific isotopes, facilities, and applications, this publication occasionally contains feature articles prepared by recognized experts on specific topics of current interest. Critical evaluations and interpretations presented are those of the editors and invited reviewers; therefore readers are encouraged to consult the original references in order to obtain all the background of the work reported and the interpretation of the results given by the original authors.

The subject headings listed below have been adopted to help maintain continuity and order, from one issue to the next, in the material reviewed. All reviews, except Feature Articles, will be arranged under these headings; but any one issue will not necessarily contain all the headings.

Isotope Production and Development	Isotopic Power Development
Isotope Technology Development	Applications in Medicine
Food Irradiation	Safety
Process Radiation Development	Isotopes Around the World
Source Development	Miscellaneous Items of Interest

P. S. Baker, Robert H. Lafferty, Jr., Martha Gerrard, D. A. Fuccillo, R. E. Greene, F. E. McKinney, and Joan E. Carden, *Editors*
A. F. Rupp, *Advisory Editor*

Oak Ridge National Laboratory

Section

I

Isotopes and Radiation Technology

General Review

This section covers several items that are too broad to be categorized in any specific subject section. First, the recently announced Isotopes Information Center at Oak Ridge National Laboratory (ORNL) is described; and then a talk given by E. E. Fowler, Director of the AEC Division of Isotopes Development, describing new developments in the isotope industry at the meeting of the Atomic Industrial Forum in Washington in November 1965, is presented.

Isotopes Information Center at ORNL

The operation of the Isotopes Information Center by Oak Ridge National Laboratory for the U. S. Atomic Energy Commission was formally announced in March 1966. This Center was established primarily to collect, evaluate, and disseminate worldwide information on the production and uses of radioisotopes in industry and research. The work of the Center in identifying, obtaining, indexing, retrieving, and correlating information on isotopes is described.

The Isotopes Information Center, operated by ORNL for AEC, was formally announced in March 1966. The organization and staffing of the Center started in July 1962, and prior to the formal announcement, most of the Center's activities were directed toward preparation and publication of *Isotopes and Radiation Technology* and acquiring and indexing sufficient information to achieve satisfactory operation of the Center.

This Center was established primarily to collect, evaluate, and disseminate worldwide information on production and uses of radioisotopes in industry and research. The Center also maintains a current awareness of uses of isotopes in biology, medicine, agriculture, and education.

Scope

The specific areas with which the Center is concerned are:

PRODUCTION

Useful Radioisotopes. Irradiation of material in reactors and accelerators; separation of radioisotopes from irradiated material; separation of fission products from reactor-irradiated uranium; preparation of transplutonium elements. (Chemical processing of irradiated uranium for uranium or plutonium recovery is excluded.)

Radioactive Sources and Irradiators. Encapsulation of radioactive sources; design of irradiators; source preparation.

Radioactive- or Stable-Isotope Targets. Preparation of targets from radioactive or enriched stable isotopes for use in accelerators and reactors.

Enrichment of Isotopes. Electromagnetic separators and separations; thermal-diffusion separations; countercurrent electromigration. (Gaseous diffusion and centrifuge separations are excluded.)

USES OF RADIOISOTOPES

In Industrial Processes or Other Areas of Technology. Radioisotope gages (density, level, thickness); process control and testing by tracer techniques; industrial radiography; leak detection; flow measurement; static elimination; luminescent paints and phosphors.

In Large-Scale Irradiations, Both Industrial and Research. Sterilization of medical products; pasteurization and sterilization of food; chemical synthesis; polymerization; textile fiber improvements; crop improvements by mutation;

insect control; sterilization of soil and sewage. Irradiations by machines as well as by radioisotopes are covered. (Destructive effects of radiation are excluded; they are covered by the Battelle Memorial Institute Radiation Effects Information Center.)

In Physical Sciences. Activation analysis; tracers in analytical chemistry and hydrology; reaction mechanisms in inorganic, physical, and organic chemistry; surveys and reviews on use of radioisotopes for dating. (Nuclear properties of isotopes are excluded; they are covered by the ORNL Nuclear Data Group and others.)

In Medicine, Agriculture, and Other Life Sciences. New uses of old isotopes; uses of new isotopes; review and summary articles; textbooks. (Routine uses of isotopes in these fields are not covered.)

In Energy Sources. Radioisotope SNAP generators for space and terrestrial uses; nuclear batteries; radioisotopic heat for uses in oceanography and desalination. (Reactor SNAP programs are excluded.)

HANDLING

Safety with Isotopes. Safe handling of isotopes; hot cells and manipulators for isotope production and use; safe shipment of isotopes; isotope-shipping-container testing. (Body accumulations, fallout, and decontamination methods are excluded.)

Detection and Determination. Unusual counting methods or new instrumentation for detection of isotopes; instruments that use isotopes in their operation. (Routine articles on calibration and uses of counters are excluded.)

Input

The scientific staff of the Center screens many types of literature to locate information that is within the Center's scope (Fig. I-1). The material scanned includes:

1. Reports of the USAEC, its contractors, and other government agencies and their contractors.
2. Reports of foreign atomic-energy installations.
3. Domestic and foreign journals.
4. Industrial bulletins.
5. Abstract journals such as *Nuclear Science Abstracts, Biological Abstracts, Chemical Abstracts, Excerpta Medica, Nuclear Science Abstracts of Japan,* and *Referativnyi Zhurnal.*
6. Book reviews and catalogs.
7. Accession lists such as those of the USAEC Division of Technical Information Extension, the International Atomic Energy Agency, Euratom, and ORNL Library.
8. Bibliographies and report lists in pertinent and fringe fields such as UKAEA *List of Publications Available to the Public,* annual review issues of *Analytical Chemistry,* and *Isotopes et Rayonnements Agriculture.*
9. News releases such as those from AEC, Oak Ridge Associated Universities, and the International Atomic Energy Agency.

Fig. I-1 Some typical documents indexed and accessioned by the Isotopes Information Center.

The scanning is greatly facilitated by a program in which the *Nuclear Science Abstracts* evaluators note papers outside their scope but of interest to the Center. The Center also exchanges information and accession lists with other information centers such as the Science Information Exchange at the Smithsonian Institution and Nondestructive Information Analysis Center of the U. S. Army Materials Research Agency, Watertown, Mass.

Indexing, Storage, and Retrieval

As a rule, in-scope reports and journal articles are obtained and stored as microfiche (Fig. I-2), and books and bibliographies are stored as full-sized copy.

Documents, when received, are read, analyzed, and indexed by scientists on the Center's staff. Indexing is by key words that answer these questions:

Which radioisotopes are discussed?
How are the isotopes produced?
What industry or science is using the isotopes?
How are the isotopes used?

Documents are also indexed by author, corporate author, report number, and title and are filed by accession numbers assigned in numerical sequence.

The Termatrex system, based on a coordinate-index, random-access plastic-card memory, is used to retrieve documents. A card is made for each indexing term, and the accession number of a document is punched into every card that has an indexing term describing the document. For retrieval all cards relevant to a particular question are superimposed on a light table, and a beam of light passes through holes indicating the numbers of the documents that contain pertinent information.

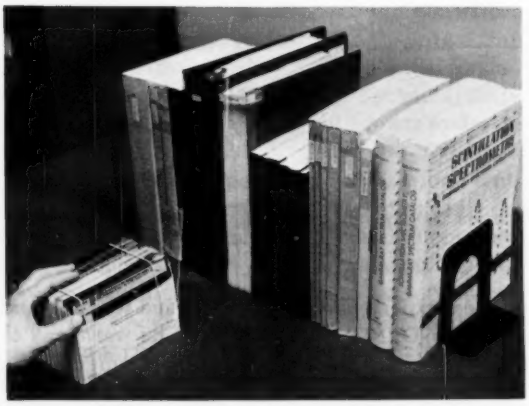


Fig. I-2 Comparison of storage space required for full-size copies of reports and microfiche copies of the same reports. The full-size copies require 1685 cu in. for storage, while the microfiche, at left, take only 90 cu in., a saving of 95% in space.

A thesaurus of key words has been developed by the staff of the Center for use in indexing and retrieving information. This list contains about 175 "acceptable" subject terms that may be used in indexing and an equal number of synonyms and related words that are not to be used but that are cross referenced to acceptable terms. Cross references to more specific and more general indexing terms are also given (Fig. I-3, page 182).

In addition to indexing with subject terms, the specific isotopes used in the paper are indexed. At present, Termatrex retrieval cards have been prepared for over 330 isotopes. Since other isotopes may not occur frequently enough to justify preparing a card for them, a Termatrex card is also made for each element. Therefore a total of approximately 600 terms—175 specific subjects, 330 isotopes, and 100 elements—is used for indexing and retrieval.

Output

The Center makes information available in the following ways (Fig. I-4, page 183):

1. Prepares for the USAEC the quarterly progress review, *Isotopes and Radiation Technology*.
2. Answers specific requests for information.
3. Issues state-of-the-art reviews on various areas of isotope applications.
4. Writes critical evaluations of various fields of isotope use and production. These reviews are prepared with particular attention to the worldwide situation.
5. Prepares special educational and informational materials, such as reports, exhibits, brochures, and pamphlets, that are used in various parts of the AEC program.
6. Exchanges information with the International Atomic Energy Agency, Eurisotop (a bureau of Euratom), The Japan Radioisotope Association, and other interested groups.

A list of publications of the Center to date is given at the end of this section.

Personnel

The Isotopes Information Center is a part of the Isotopes Division at ORNL, and Philip S.

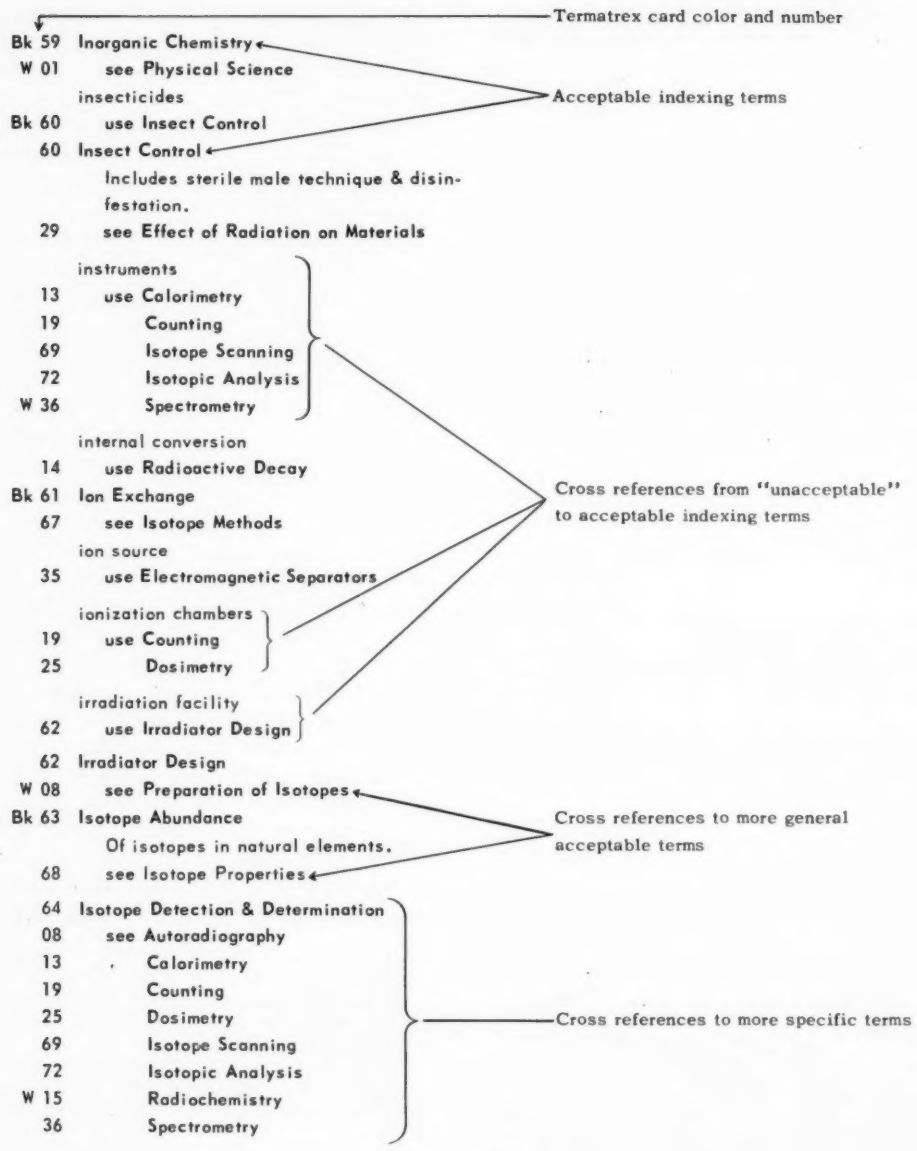


Fig. I-3 Sample of Isotopes Information Center key word list.

Baker, Assistant Superintendent of the Isotopes Division, is Director of the Center. The Center's staff was selected to bring a wide variety of backgrounds, training, and experience into the work.

P. S. Baker, a graduate of DePauw University, received an A.M. degree from the University of Arkansas and a Ph.D. degree in inorganic chemistry from the University of Illinois. After a varied experience in industry and teaching, he came to ORNL in 1952, where he was Head of the Chemistry Department of the former Stable Isotopes Division. When this Division became part of the present Isotopes Division, Dr. Baker became Superintendent of the Electromagnetic Separations Department and then, successively, Superintendent of the Isotopes Sales Department, Superintendent of the Advanced Isotopes Devel-

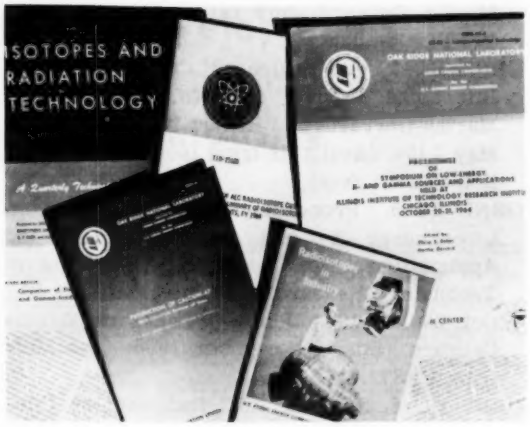


Fig. I-4 Some output of the Isotopes Information Center.

opment Department, and Assistant Superintendent of the Isotopes Division.

The other five members of the scientific and technical staff are:

Robert H. Lafferty, Jr., a graduate of Davidson College, Davidson, N. C., received a Ph.D. degree in analytical chemistry from Cornell University. After two years of teaching at Lehigh University, he joined the Manhattan Project on the staff of the Kellex Corporation, the architect–engineer of the gaseous diffusion plant in Oak Ridge, as a research chemist. In 1945 he was employed by Union Carbide Corporation at the Oak Ridge Gaseous Diffusion Plant. After several years as Head of the Analytical and Fluorocarbon Section of the Chemical Research Department, he became technical assistant to the Superintendent of the Technical Division, a position that he held until his transfer to the Isotopes Information Center at ORNL in 1962. At the Oak Ridge Gaseous Diffusion Plant, Dr. Lafferty had a wide variety of experience with fluorine and uranium analytical chemistry, isotope separations by many methods, fluorocarbon chemistry, and nuclear safety work.

Martha Gerrard, with an A.B. and M.S. degree in chemistry and physics, did graduate work in biochemistry at Cornell University. After teaching chemistry, working as a research assistant, and editing technical books for McGraw-Hill Book Company in their New York office, she came to Oak Ridge on the National Nuclear Energy Series project. Mrs. Gerrard joined the Oak Ridge National Laboratory in 1950 and was a technical editor and writer in the Chemical Technology Division before transferring to the Information Center staff in October 1962. In 1958, on leave of absence, she was a technical editor for the United Nations in Geneva on the Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. She currently contributes to the ORNL translation program and, off-duty, abstracts English, Russian, French, Italian, Spanish, Czech, and German papers for *Chemical Abstracts*.

Domenic A. Fuccillo, Jr., holds an A.B. degree in zoology and a B.J. degree in journalism from the University of Missouri. After four years in the Air Force as an electronics technician, he was a newspaper reporter and then started as a technical writer with a computer firm on the west coast. Mr. Fuccillo came to ORNL in 1960 as a technical editor in the Biology Division and transferred to the Isotopes Information Center in late 1963.

Ralph E. Greene, who received an A.B. degree in chemistry from Augustana College, Rock Island, Ill., worked four years at Rock Island Arsenal before joining the Union Carbide Corporation in 1945 at the Oak Ridge Gaseous Diffusion Plant. He worked in the fission counting laboratory and later was Head of the Uranium Isotopes Standards Section. This Section prepared precise isotope uranium standards for the evaluation of plant performance and for the sale and accountability of uranium. This group also prepared electrodeposited sources of essentially pure isotopes of uranium for physics research at many atomic installations throughout the country and did development work in radiochemical methods for uranium, counting methods, solvent extraction, and fluorination of uranium. In 1956 Mr. Greene became technical assistant to the Superintendent of the Analytical Laboratories, and in July 1964 he joined the Isotopes Information Center.

Francis E. McKinney received a B.S. degree in mathematics from Auburn University and is currently writing his Master's thesis in English literature for the same university. While an undergraduate at Auburn, Mr. McKinney was a co-op student with NASA at Marshall Space Flight Center, and following his graduation he worked at Huntsville as a mathematician. Prior to joining the Information Center in June 1965, he taught freshman English composition at Auburn.

How To Contact

The Center attempts to answer all reasonable questions within the capabilities of its system. Requests for information may be made by telephone, correspondence, or a visit to the Center. Telephone calls should be directed to Area Code 615, Phone 483-8611, Extension 3-1742. For those who have access to the Federal Telecommunications System, the number is 615-483-1742.

Written requests should be addressed to P. S. Baker, Director, Isotopes Information Center, Oak Ridge National Laboratory, Post Office Box X, Oak Ridge, Tenn. 37830.

The Center is open from 8:00 a.m. to 4:30 p.m., Monday through Friday; although no appointment is necessary, prior notice of a visit will result in more efficient use of time during the visit.

Your Help

The quality of service that the Center gives will depend mainly on the quality and coverage of papers that are in the Center's system. Scientists and engineers who are using radioisotopes in their work are requested to send current reprints as well as reprints describing earlier work to the Center at the above address.

Review articles on the production or use of radioisotopes are solicited for publication in *Isotopes and Radiation Technology*. Any information about computer codes for isotope production or other related calculations is welcome.

(Robert H. Lafferty, Jr.)

Publications by Isotopes Information Center

The Center has published the following reports, or Center personnel have made major contributions to their preparation:

Isotopes and Radiation Technology, a quarterly Technical Progress Review published by the U. S. Atomic Energy Commission. (Available from the Superintendent of Documents, U. S. Government Printing Office, Washington 20402; subscription $2.50 per year, $0.70 for individual issue)

ORNL-IIC-1, Publications on Isotopes at Oak Ridge National Laboratory, 1946–1963, Robert H. Lafferty, Jr., P. S. Baker, and Martha Gerrard, July 1964. (Available from CFSTI,* $4.00)

ORNL-IIC-2, Production of Calcium-47, with Literature Review of Uses, P. S. Baker, Martha Gerrard, and Robert H. Lafferty, Jr., May 1964. (Available from Isotopes Information Center, free)

ORNL-IIC-5, Proceedings of Symposium on Low-Energy X- and Gamma Sources and Applications, Held at Illinois Institute of Technology Research Institute, Chicago, Ill., Oct. 20–21, 1964, Philip S. Baker and Martha Gerrard (Eds.), November 1965. (Available from CFSTI,* $4.00)

ORNL-IIC-6, List of AEC Radioisotope Customers with Summary of Radioisotope Shipments, FY 1965, P. S. Baker, March 1966. (Available from CFSTI,* $3.00)

ORNL-IIC-7, Proceedings of Information Meeting on Irradiated Wood–Plastic Materials Held at Conrad Hilton Hotel, Chicago, Ill., Sept. 15, 1965, R. E. Greene and P. S. Baker (Eds.), March 1966. (Available from CFSTI,* $2.00)

TID-21620, List of AEC Radioisotope Customers with Summary of Radioisotope Shipments, FY 1964, P. S. Baker, March 1965. (Available from CFSTI,* $3.00)

Radioisotopes in Industry, P. S. Baker, D. A. Fuccillo, Jr., Martha Gerrard, and Robert H. Lafferty, Jr., November 1965. (One of the USAEC's Understanding the Atom Series.) (Available from USAEC Division of Technical Information Extension, P. O. Box 62, Oak Ridge, Tennessee 37830, free)

ORNL-TM-1356, Selected Abstracts of Non-U. S. Literature on Production and Industrial Uses of Radioisotopes, Martha Gerrard, P. S. Baker, and Robert H. Lafferty, Jr., January 1966. (Available from Isotopes Information Center, free)

ORNL-TM-1356, Suppl. 1, Selected Abstracts of Non-U. S. Literature on Production and Industrial Uses of Radioisotopes, Martha Gerrard, P. S. Baker, and Robert H. Lafferty, Jr., March 1966. (Available from Isotopes Information Center, free)

ORNL-3633, ORNL Radioisotopes Procedures Manual, coordinated by F. N. Case; compiled by D. A. Fuccillo, Jr., and Sylvia B. Ewing, June 1964. (Available from CFSTI,* $3.00)

*Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Virginia 22151.

New Developments and Trends in the Isotope Industry*†

By E. E. Fowler‡

It can be said without qualification that the prospects for an increased growth rate in the application of isotopes and radiation have never been brighter in the United States than they are today. Parallel improvements and expansion in utilization of isotopes and radiation have taken place in all fields of industrial application. The growth pattern has been both constant and healthy. The expansion has occurred in a competitive environment, with increasing use being made in areas of vigorous industrial development.

To assist AEC in assessing growth and trends in the isotopes and radiation industry, two independent studies were initiated during the past year. The first of these studies, carried out by the Arthur D. Little Company under contract to AEC,[1] updated an earlier review conducted for AEC in 1958 by the National Industrial Conference Board.[2] Twenty-one major industrial areas were investigated, and some 200 persons representing 133 industrial, academic, and government organizations were interviewed to determine how isotopes and radiation are being used; future trends were assessed. The picture was broadly encouraging for future development and use of isotopes and radiation.

Another more specialized and limited study was conducted by Lauchlin M. Currie, Chairman of the AEC's Advisory Committee on Isotopes and Radiation Development, and O. M. Bizzell, Chief of the Technology Utilization Branch, Division of Isotopes Development, AEC. The study was designed to (1) determine the extent of industrial development of isotopes and radiation now in progress or being planned, (2) identify factors that limit their use, and (3) obtain recommendations on how AEC might enhance development of this part of the atomic-energy program. Forty companies were visited, including large and small users interested in various applications of isotopes and radiation and scattered throughout all major U. S. industrial sectors. The industry indicated that the potential for expansion of routine applications of isotopes and radiation is large and that the present rate of growth in industrial uses of isotopes—said to be between 3 and 5% per year—could reach 15 to 20% per year under a vigorous AEC–industry cooperative isotope and radiation demonstration program. Of the 40 firms visited, 93% foresaw greater use of isotopes in their companies in the next five years, and 43% expected this increased usage to be substantial; only 3% reported a decreasing trend in use.

Additionally the report prepared by Currie set forth specific industry recommendations, which included:

1. Actively seeking joint funding projects for isotopes and radiation developments with industry.
2. Setting up procedures for loan or rental of large radiation sources.
3. Broadening AEC patent procedures.
4. Extending the use of the general licensing provision of AEC regulations in light of past experience.
5. Adopting more positive public-information programs to offset unfounded fears about isotopes and radiation.

The AEC and its Advisory Committee on Isotopes and Radiation Development have the Currie report under study to determine how the findings can be translated into policy that would improve prospects for further expansion of industrial applications of isotopes and radiation.

Growth Statistics

I would like to illustrate the dimensions of the growth of the industrial use of isotopes and radiation in the United States with historical statistics. In Fig. I-5 we see the pattern of growth of U. S. commercial supply of isotopes from 1956 to 1964, based on Bureau of Census statistics. Sales of isotopes in 1964 were approximately $7.75 million. As a consequence of AEC policy of transferring radioisotope production to commercial facilities whenever possible, this growth represents primarily sales by

*Covers material in talk presented at the Atomic Industrial Forum Twelfth Annual Conference, Washington, D. C., Nov. 17, 1965.

†The views expressed in this article do not necessarily represent those of the U. S. Atomic Energy Commission or its appropriate office or division.

‡Director, Division of Isotopes Development, U. S. Atomic Energy Commission, Washington, D. C.

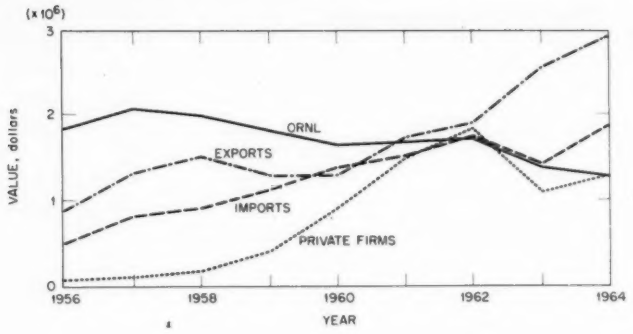


Fig. I-5 Pattern of U. S. radioisotope supply.

private firms and imports. The 1963 dip in private sales is attributable to some redefinition of items included and perhaps incomplete reporting to the Bureau of Census.

Figure I-6 shows the distribution of organizations and individuals licensed by AEC to use radioisotopes as of September 1965. Medical institutions and physicians lead in number of users, followed by industrial firms, government (state and federal) laboratories, colleges, and universities. It is interesting that the same "sequence-in-use" among medical, industrial, and all other users has existed essentially since the beginning of the U. S. program of production and distribution of radioisotopes in 1946.

Figure I-7 indicates the growth since 1946 in the number of industrial firms licensed to use radioisotopes. For the 10 years following 1952, the number increased at a nearly constant rate of about 170 per year. The more rapid increase beginning in 1962 may be due in part to the transfer of licensing authority from AEC to an increasing number of state-government regulatory authorities, currently numbering 11.

The growth of radioisotope use by companies in various categories indicates that the largest group—industrial radiographers, testing laboratories, and research firms—has tripled over the last five years. The chemical industry is

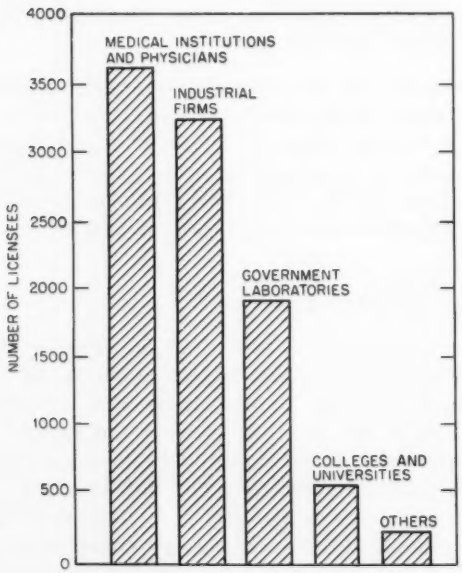


Fig. I-6 Radioisotope licensees by category, September 1965.

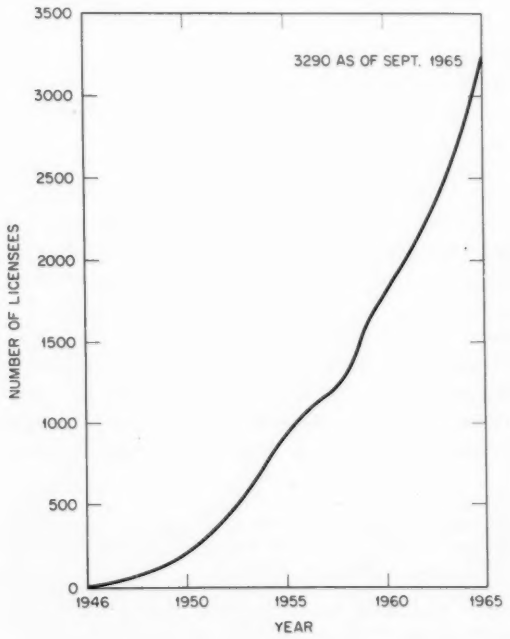


Fig. I-7 Growth of industrial users of radioisotopes.

second in the number of users, with an equally substantial growth rate. The other industries in the top five are: primary metal products, paper and allied products, and fabricated metal products.

Looking at the types of applications being made by these industries, we find that radioisotope thickness gages[3] are used most extensively by the paper, plastics, primary metals, and rubber industries. Radioisotope density gages[3,4] find wider application in the chemical, paper, stone, clay, glass, petroleum refining, and mining industries. Nearly the same pattern is found for isotope level gages,[3] with significant use also in the plastics industry. Gamma radiography[5] is concentrated largely in engineering and architectural services, including primary metals, fabricated metal products, transportation equipment, and nonelectrical machinery.

Radioisotope tracer techniques[6] are most widely used in the chemical, crude petroleum, natural gas, electrical machinery, and pharmaceutical industries. These statistics indicate the magnitude and direction of growth of radioisotope use by industry in the United States, but they do not present a full picture. Let us then examine the effect of trends in technology to obtain a more complete understanding of the movement of industrial applications of radioisotopes in the United States.

TRACER METHODOLOGY AND APPLICATIONS

Of the classical industrial applications of radioisotopes — tracing, gaging, and radiography — tracer applications appear to provide the greatest potential for expansion during the period between now and the mid-1970's. The ultimate dimension and economic meaning of industrial tracer applications of radioisotopes are clearly indefinable today, but developments will continue which will put radioisotopes to work as tracers on more and more industrial problems. Contributing to this will be the increasing importance of radioanalytical methods. In the United States we are devoting considerable effort to development of rapid, sensitive radioanalytical techniques such as "activation tracing," which involves the use of stable tracers followed by neutron or charged-particle activation analysis to measure the stable tracer concentration. While the potential is good, achievement of widespread industrial use of tracer methods for process-control purposes will require considerable development and refinement of analytical measurement techniques as well as custom tailoring to particular processes.

RADIOISOTOPE GAGING

In the use of radioisotope gages for process control of manufactured products, the trend continues to be toward automation. Within a relatively short time, we have progressed from the rather crude first-generation radioisotope gaging devices to highly automated systems that collect, store, and analyze many kinds of production data essential to the efficient, economic manufacturing of a wide spectrum of products. American industry has invested some $100 million in radioisotope gaging systems; this investment in isotope gages is saving this same industry approximately $500 million annually in manufacturing operations.

The extent of use of isotope gages varies from industry to industry. Of the approximately 1500 paper machines operating in the United States today, it is somewhat surprising that only about 220 are equipped with radioisotope beta gages. Therefore a good potential exists for future growth in gaging use in this industry. In some other industries, however, the use of isotope gages is more widespread, and growth is likely to be tied to the expansion of the industry as a whole. For example, it is estimated that more than 95% of the rubber currently produced for automobile tires is measured by radioisotope gages. Likewise, in the tobacco industry, nearly 80% of the cigarettes produced in the United States are manufactured using isotope gages. About 2500 such gages are in use today — only a few more than five years ago — which indicates near saturation of this particular industry. Growth in sheet gaging is likely to be most impressive in relatively modern industries such as plastics, where sophisticated instrumentation is accepted and production equipment can be readily adapted for automatic control.

RADIOGRAPHY

It is not to be expected that we will experience a large continuing growth in the use of radioisotopes for industrial radiography. I would expect essentially a steady state to exist. New technology or markets do not appear to be de-

veloping which would alter current use significantly.

However, definite trends are apparent in equipment design, as well as source size and intensity. These trends are toward more-portable equipment, achievement of smaller focal spots, and the use of larger sources with higher specific activity. Portability is a major advantage of radioisotope units over X-ray units, and this advantage is being exploited as much as possible. A major factor contributing to decreased weight and size of radiographic devices is the use of depleted uranium, instead of lead, as shielding material.

Future Trends

At this point it is proper to examine the prospect for major changes in the use of radioisotopes, and I hold that the prospects are good. While it can be expected that radioisotopes will experience overall growth in the classical areas of use over the next 10 years, there is little reason to believe that the rate of this growth will be much different from that over the past few years. Therefore the economic contribution from radioisotope use in industry will increase at the same rate with little expectation of any gross upward change. If there is a major change, it will occur, not through the classic applications, but through development of broad new areas of technology. Here, then, rest both the stricture and the challenge for greatly expanding the productive use of radioisotopes and their economic contribution. Good technical reasons exist now to indicate that this next stage in radioisotope use will occur in the broad application of massive quantities of radioisotopes for radiation or for sources whose heat is converted to electric power or used directly.

Not only will successful development of this technology give a totally new dimension to radioisotope use; it will also effectively create a new radioisotope industry. I visualize a radiation industry associated with:

1. Radiation processing for production of new products unique to radiation.
2. Preservation of foods.
3. Design and manufacture of devices using radioisotopes as heat sources for electric-power production and for direct use of the heat.

For these industries there will be required the ancillary industries for production of massive quantities of radioisotopes and fission products and for design and construction of equipment and facilities to support them.

I would like to examine in somewhat greater detail why it is reasonable to expect a new dimension in radioisotope use and, for this purpose, to discuss briefly the areas that I have just identified.

PROCESS RADIATION DEVELOPMENT

Contrasted to the slow initial start in process radiation, today I believe we are witnessing new gains, new interests, and new efforts in developing ionizing radiation for process purposes. An estimated 300 kw of installed radiation power is now being used in the United States for commercial irradiation purposes. Two years ago it was estimated that industrial radiation processing amounted to a $70 million annual business in the United States. Since then there has been a marked upswing in actual and planned investment and operation, particularly in irradiation of polymers to modify their properties, sterilization of medical supplies,[7] and production of biodegradable detergents. For example, it is estimated that about $20 million worth of cross-linked plastic insulation products was manufactured in 1964. Recently one large producer of telephone cable indicated a requirement for about 400 million 1-in.-diameter cable connectors per year, made of irradiated polyolefin tubing. Radiation production of heat-shrinkable polyethylene film for packaging is a small but rapidly growing business with annual sales of about $6 million and a volume expected to grow at a rate of about 25% per year for the next several years. Two new radioisotope facilities for sterilization of medical supplies have gone on stream in the United States during the past 18 months.

Healthy private interest is also evident in new areas of process radiation application such as AEC's development program on wood–plastic materials.[8] Two private companies have been established specifically for commercializing wood–plastics technology, and a third company is providing impregnation and irradiation services. Another good sign is the response of the wood products industry to an open invitation by AEC to join in a cooperative evaluation program for wood–plastic materials. We were gratified that 187 companies responded to the invitation. All were sincerely interested in participating,

but money limitations forced us to choose only 78 for the evaluation program. Selections were made primarily on the basis of avoiding duplication of products and potential economic importance of selected manufactured products. The AEC's costs for this effort will amount to about $40,000, while industry will invest perhaps four times this amount in fabricating the test products and performing the evaluations, the results of which will be made publicly available.

Increased Cobalt-60 Production.[9] Another barometer of increasing interest in process radiation development is the AEC backlog of orders for large quantities of ^{60}Co. Production of ^{60}Co has been increased at the Commission's Savannah River plant and limited production started at the Richland, Wash., plant to meet a growing demand for large quantities of this radioisotope. Of the nearly 16 million curies being produced or planned for production, over 3 million curies is for commercial orders with the remaining 12 to 13 million curies earmarked for government projects.

Cobalt-60 Price Change. The Commission has just publicly announced a change in its price schedule for ^{60}Co. The pricing policy has been under active review for the past 12 to 15 months, during which time the views of all interested segments of industry have been sought. The new schedule, effective Dec. 18, 1965, makes two major changes in the existing price structure, which was set in 1963:

1. The price on low-specific-activity material is decreased from 50 to 40 cents per curie on material with a specific activity of up to 15 curies/g.

2. The maximum limit on specific activity of material that the Commission will supply is raised from the present 30 curies/g to 45 curies/g. In this specific activity range, ^{60}Co will be supplied only in the form of strips, known as "BNL strips." The Commission will not supply ^{60}Co in quantities less than 100,000 curies if commercial producers can meet the requirements of an order under reasonable conditions of time, quality of product, or price. The new schedule is designed to encourage development of large-scale industrial applications of ^{60}Co and, hopefully, will permit American firms to compete more effectively in world markets for radiation installations.

Reduced Prices of Fission Products. Another significant development important to the process radiation industry is the plan of Isochem, Inc., to build a plant at Richland, Wash., for production and encapsulation of the fission products ^{90}Sr, ^{147}Pm, ^{144}Ce, and ^{137}Cs. I would like to note, moreover, that on Nov. 10, 1965, the Commission effected sharp price reductions on these four isotopes to encourage the development of uses and markets during the time between now and the operational availability of the Ioschem plant in 1968. The new prices for large amounts of ^{90}Sr and ^{147}Pm are 20 cents per curie; for ^{144}Ce, 15 cents per curie; and for ^{137}Cs, 12.5 cents per curie. The AEC will, of course, continue to supply fission products until the new fission-product plant comes on line.

HIRDL Available to Industry. I also wish to announce another step by AEC to encourage industry to take a more active role in developing new methods for using radiation on a commercial basis. The High Intensity Radiation Development Laboratory (HIRDL)[10] located at Brookhaven National Laboratory is now being made available to industry, as well as to other organizations, to conduct their own research and development while retaining their proprietary interests. This is an opportunity for industry to make use of the largest process radiation facility in the world, and we hope that many will take advantage of it.

RADIATION PRESERVATION OF FOOD

We are particularly encouraged in the United States today with the progress we are making in the development of radiation processing of food.[11] I believe that there is every technical and economic reason to indicate that we will be successful in developing the first completely new food processing method in 150 years. The practical consequences of radiation processing of foods will be the opening up of new markets by virtue of the longer marketing times of perishable foods, food products of high quality, and reduction in spoilage losses.

As most of you know, we have two major food preservation programs in the United States. One is being carried out by the U. S. Department of the Army and is devoted to establishing successfully a technology for radiation sterilization of foods for long-term storage without refrigeration. The other program, under the sponsorship of AEC, is directed toward establishment of a

technology for radiation pasteurization of perishable foods to extend their marketable time. Foods processed in this latter manner must be maintained under refrigerated conditions.

Both programs have emerged from an intensive research phase into what might be called a product-development phase. Obtaining Food and Drug Administration clearances on a variety of individual food products for general human consumption remains the principal hurdle before the process can be commercialized. Procedures for obtaining clearances are lengthy and complicated. We are proceeding with the confidence that we will be successful in developing needed scientific and technical data for the clearances and that all other obstacles to commercialization will be removed by that time through combined industry–government efforts. Several joint projects are already under way to achieve this goal. We have invited the fisheries industry to join us in the use of the new Marine Products Development Irradiator at Gloucester, Mass., to conduct large-scale shipping, storage, and laboratory tests on a wide variety of radiation-processed marine products. Some 20 commercial firms have responded to this invitation; this we find very gratifying. Such a cooperative effort is, we believe, mutually beneficial to AEC and industry since we, in the government, can take advantage of commercial experience and facilities in carrying out the large-scale tests, and industry benefits by direct experience with this new food-processing method. In addition, we will soon have available a large portable irradiator, which will be offered to industry for use in developmental processing of fresh fruits and vegetables. Another transportable irradiator of smaller size will travel around the country to process test quantities of all types of foods. In each case AEC will ask only for the evaluations in return for use of the irradiators.

Commercial Meat Irradiator. The Department of Defense and AEC have already publicly announced their desire to see private construction and operation of a pilot meat-sterilization plant with a capacity of a million pounds per year. The armed services are prepared to guarantee the purchase of a portion of the output of the plant for at least three years, and AEC has expressed a willingness to assist by providing design money and the radiation source, if necessary. An interagency task force has been established to visit some 25 meat-packaging, equipment, and nuclear companies that have indicated an interest in the proposal to determine whether or not an arrangement can be worked out to bring into operation within the next two years the world's first pilot-plant meat irradiator.

ISOTOPIC POWER

One of the most important new areas of radioisotope application in recent years is based on the process of radioisotope decay, in which thermal energy is liberated at a rate and over a period of time characteristic of the isotope. This has given rise to the development of small nuclear electric-power supplies, which derive their energy from radioisotope decay, for use in locations and under environments where more conventional sources of electric power are unsatisfactory.

Already isotopic power systems are being used to provide auxiliary electric power for navigational satellites in space, remote automatic weather stations near both the North and South Poles, and navigational buoys. In the near future it is anticipated that other isotopic devices will power lunar scientific probes; communications and meteorological satellites; manned spacecraft; and a host of additional terrestrial, marine, and space systems.[12] Additionally, good technical prospects exist for successful development of an entire spectrum of nonelectric-power applications of radioisotopes in space. Research and development programs are under way which are designed to make available the benefits of radioisotope technology to the U. S. space program. These include applications such as propulsion systems, temperature-control devices, and life-support systems.

To examine the economic consequences of this developing technology, let us consider those areas of greatest importance—production of materials and manufacture of devices. Present indications are that by the early 1970's hundreds of thermal kilowatts or more of radioisotope power will be required. The extremely large quantity of radioisotope material that will be required to satisfy isotopic power and heat-source needs has posed the most severe challenge to U. S. production of radioisotopes that it has yet faced. Isotopic power fuels are currently being produced at sites operated by AEC. However, industry is being encouraged to take

an increasingly active part in these production activities. An important step in this direction is the planned investment of some $8 million by Isochem, Inc., for the private construction of the fission-product plant mentioned above. It is also expected that, as the civilian power economy develops and matures, important consideration will be given to isotope needs by the use of this capability.

In addition to fission products, other radioisotopes, e.g., ^{210}Po, ^{242}Cm, ^{244}Cm, ^{60}Co, and ^{238}Pu, have important applications as heat sources, either for electric-power production or for direct use of the thermal energy.

Under a fully developed use of radioisotopes as electric-power and heat sources, we can contemplate an annual radioisotope production and fuels business approaching $100 million.

Based on current plans AEC will spend, during the present fiscal year, approximately $18 million on the development of prototype isotopic power hardware and fuels for a variety of terrestrial, oceanographic, and space applications. Other U. S. government agencies, e.g., the National Aeronautics and Space Administration and the Department of Defense, also have programs related to isotopic power devices. We anticipate that these development programs will give rise to a new economically important segment of the radioisotope industry concerned with the manufacture of isotopic power equipment measured in tens of millions of dollars annually.

Conclusion

In conclusion I wish to state that the advances in isotope and radiation development over the recent past have been outstanding. At the same time we recognize that our biggest job is ahead of us. In the near future we can expect to see multimegacuries of individual isotopes used in radiation processing, in electric-power generators, and for space propulsion and direct heat applications. There will be new and exciting basic discoveries, expanded and improved routine uses, and instrumented systems developed using radioisotopes for explorations from the ocean floor to outer space — at the extremes of our environment.

It is clear that, to achieve a marked increase in our rate of progress, it is incumbent upon us to develop a partnership between government and industry in isotopes and radiation development which makes maximum use of resources, human and financial, available to both.

References

New Developments and Trends in the Isotope Industry

1. E. W. Stone, J. H. B. George, and H. P. Beutner, Isotopes in Industry. Trends in the Industrial Use of Radioisotopes and Ionizing Radiation, USAEC Report NYO-3337-16, Arthur D. Little, Inc., Sept. 24, 1965.
2. J. J. McMahon and A. Berman, Radioisotopes in Industry, USAEC Report NYO-2977, National Industrial Conference Board, Inc., November 1959.
3. Radioisotope Measurement and Control Systems, *Isotopes Radiation Technol.*, 1(2): 160-174, 177-179 (Winter 1963–1964).
4. *a.* J. L. Smith and D. W. Willen, Radio-Snow Gages: A Review of the Literature, *Isotopes Radiation Technol.*, 2(1): 41-49 (Fall 1964).
   b. W. A. Mercer and J. W. Ralls, Use of Isotopes in the Food-Canning Industry, *Isotopes Radiation Technol.*, 1(3): 245-255 (especially 245-246), 274 (Spring 1964).
   c. Measurement of Riverbed Variation, *Isotopes Radiation Technol.*, 2(2): 140 (Winter 1964–1965).
5. Source Development, *Isotopes Radiation Technol.*, 2(1): 55-71 (Fall 1964); 2(3): 274-275 (Spring 1965).
6. *a.* Radioactive Tracer Uses in the Mining Industry, *Isotopes Radiation Technol.*, 2(1): 18-34, 47-48 (Fall 1964).
   b. Isotope Technology Development, *Isotopes Radiation Technol.*, 2(2): 124-140, 146-147 (Winter 1964–1965).
   c. F. E. Armstrong and W. D. Howell, Recent Advances in Radioisotope Applications for the Exploitation of Petroleum and Natural-Gas Reservoirs, *Isotopes Radiation Technol.*, 3(2): 102-110 (Winter 1965–1966).
7. C. Artandi and W. Van Winkle, Jr., Comparison of Electron-Beam and Gamma-Irradiation Plants, *Isotopes Radiation Technol.*, 2(4): 321-328 (Summer 1965).
8. *a.* E. E. Fowler and P. C. Aebersold, Status of the U. S. Program on Isotopes and Radiation Development, *Isotopes Radiation Technol.*, 1(1): 1-26 (especially 13-14) (Fall 1963).
   b. D. S. Ballantine, Use of Gamma Radiation To Produce Wood–Plastic Combinations, *Isotopes Radiation Technol.*, 1(2): 189-195 (Winter 1963–1964).
   c. J. E. Machurek, G. R. Dietz, and M. H. Stein, Current Status and Future Prospects for Commercial Radiation Processing, *Isotopes Radiation Technol.*, 2(3): 260-266 (especially 263-264) (Spring 1965).
   d. D. A. Fuccillo, Radiation-Induced Polymerization, *Isotopes Radiation Technol.*, 3(1): 49-58, 63-65 (Fall 1965); 3(3) (in press).
9. *a.* A. H. Dexter, ^{60}Co Heat Sources for 10-60 kw(e) Generators, USAEC Report DP-974, Savannah River Laboratory, July 1965.
   b. J. W. Joseph, Jr., H. F. Allen, C. L. Auger-

man, and A. H. Dexter, Radioactive Cobalt for Heat Sources, USAEC Report DP-1012, Savannah River Laboratory, October 1965.

10. F. X. Rizzo, Radiation Engineering Activities at Brookhaven National Laboratory, *Isotopes Radiation Technol.*, 1(1): 78-83 (Fall 1963).
11. *a.* E. C. Maxie, N. F. Sommer, and H. L. Rae, Effect of Gamma Irradiation on Shasta Strawberries Under Marketing Conditions, *Isotopes Radiation Technol.*, 2(1): 50-54 (Fall 1964).
    b. K. G. Shea, AEC Program on Low-Dose Irradiation Processing of Food, *Isotopes Radiation Technol.*, 1(2): 181-188 (Winter 1963–1964).
    c. Food Irradiation, *Isotopes Radiation Technol.*, 3(1): 30-48 (Fall 1965).
12. *a.* Radioisotope Power Sources, *Isotopes Radiation Technol.*, 1(1): 89-91, 95-96 (Fall 1963).
    b. G. A. Fowler, Aerospace Safety of Isotopic and Reactor Power Sources, *Isotopes Radiation Technol.*, 2(4): 350-355 (Summer 1965).
    c. Isotopic Power Development, *Isotopes Radiation Technol.*, 1(4): 325-339 (Summer 1964).

Section

II

Isotopes and Radiation Technology

Isotope Production and Development

The electromagnetic separation of stable isotopes, which are used primarily in making targets for physical measurements and for radioisotope manufacture, was reviewed earlier.[1] In this issue we present the first in a series of reviews on chemical purification methods used at Oak Ridge National Laboratory for calutron-separated stable isotopes and a review of the literature on the photochemical separation method.

The Chemistry of Electromagnetically Separated Stable Isotopes

The chemistry associated with the recovery of enriched electromagnetically separated isotopes at Oak Ridge National Laboratory is described. The general considerations of problems inherent in the handling and analysis of these materials are discussed, and a brief description of the chemistry of charge materials is given. In this first of a series of articles, the chemical purification methods for strontium, barium, and lead based upon the insolubility of their nitrate salts in strong nitric acid and for zirconium and hafnium with DL*-mandelic acid are described.*

In the introductory section of this review of the chemistry of the recovery and purification of enriched stable isotopes made available by electromagnetic separation, some of the problems inherent in the handling and analysis of these costly enriched isotopes are discussed. The chemistry of charge materials is briefly mentioned, and the purification methods for isotopes of strontium, barium, lead, zirconium, and hafnium are described. The purification methods for enriched isotopes of other elements will appear in subsequent issues. A brief compilation of purification methods has been reported by Weaver,[2] and the electromagnetic-separation process, chemical problems involved in processing isotopic concentrates, and the uses of enriched stable isotopes have been described elsewhere.[1,3,4]

General Considerations

The overall process for the electromagnetic separation of stable isotopes involves much more than the mere separation of different masses and their collection in suitable "pockets." * Before the actual separation can begin, considerable effort is often required to provide suitable "charge material" for the separation step. Not only must the charge be relatively pure chemically, but also it must be in a form that can be satisfactorily vaporized and ionized. Weaver[5] and Sheridan, Gwinn, and Love[6] have described the preparation of charge materials.

Some starting materials that formerly required purification, e.g., $FeCl_2$ and the rare-earth oxides, are now commercially available in pure enough form to be used without treatment. However, many elements must be converted to forms not routinely available. For example, $CrCl_3$ is prepared by thermal decomposition of $(NH_4)_2Cr_2O_7$ followed by thermal conversion of the resulting oxide to $CrCl_3$ by means of CCl_4, and more recently the chlorination step has been carried out directly in the calutron;[7] GeS_2 by treating $GeCl_4$ with $(NH_4)_2S$; OsO_4 by heating osmium metal with oxygen; S_2Cl_2 by chlorinating sulfur; VF_3 by heating V_2O_3 with NH_4HF_2 (Ref. 8); and the rare-earth

*Graphite and copper are common pocket materials, but aluminum, silver, and stainless steel are also used. Magnesium, cadmium, or copper oxide are also frequently placed within the pocket to increase retention.

chlorides by high-temperature treatment of the oxides with CCl_4.

Enriched stable isotopes, because of the electromagnetic-separation time involved, are in some instances extremely costly; they may have values ranging from a few cents to several hundred dollars per milligram ($0.01/mg is $4500/lb). Therefore quantitative recovery is essential. Since high chemical purity is also desirable, the problem arises of trying to combine essentially quantitative recovery with a high degree of purity. Either goal can be rather readily achieved at the expense of the other, but the problem becomes much more difficult when both are required. To add to the difficulty, the sometimes lengthy purification procedure must be performed separately for *each* recovered isotope of a given element. (The number of isotopes varies all the way from 2 for such elements as chlorine, bromine, and silver to 10 for tin.) The magnitude of the problem is indicated by the frequency distribution of isotopes of 53 elements that are separated electromagnetically:

No. of stable isotopes per element	No. of elements	No. of stable isotopes per element	No. of elements
2	18	7	10
3	3	8	2
4	6	9	0
5	6	10	1
6	7		

From these 53 elements almost 240 individual isotopes must be prepared. In addition, different "runs" usually give different degrees of enrichment; thus separate purifications are also required for different concentrations of the same isotope.

Natural isotope abundances range from less than 0.01 to nearly 100%; therefore the quantity of the separated isotope in each of the various receiver pockets may vary from milligrams to more than a hundred grams, depending on the particular isotopic abundance. Obviously the chemical separation procedures and equipment must be adapted to handle the specific quantity of each collected isotope.

Product Purification

The deposit in each mass pocket must be converted to a useful, pure material of known chemical and isotopic composition. For each isotope this involves chemical removal from the pocket material, chemical purification, conversion to a stable inventory form, and chemical and isotopic analysis.

IMPURITIES

One purification step is begun prior to the separation process, i.e., purification of graphite receivers, or "pockets." Graphite purification has been developed to the degree that the impurities contributed from this source (calcium, silicon, and iron, for example) are no longer significant in the final product. When copper receivers are used, the copper dissolved during the removal of the sample from the receiver may be separated by electrolysis or by ion-exchange techniques.

The electromagnetic separation is in itself a purification method, since, for the most part, only those ions with masses in a very limited range are collected in any one pocket. One isotope of calcium, ^{40}Ca, which is approximately 97% abundant and therefore collected in relatively large quantities during the enrichment of the other calcium isotopes, is of sufficient purity to be used as a spectrochemical standard[9] because it contains much lower concentrations of the impurities that are difficult or almost impossible to remove by the traditional chemical methods. Rains, Zittel, and Ferguson[10] have modified a method developed by Farmer[11] and reported by Mitchell[12] that gives good chemical separation of calcium from strontium.

During the purification of the individual isotopes, small amounts of two types of impurities can be introduced: (1) foreign elements, or (2) the element being processed, but with different (including natural) isotopic composition. Thus introduction of impurities from reagents, distilled water, containers, and apparatus must be prevented wherever possible. In one instance a separated lithium isotope apparently was contaminated by traces of natural lithium in the air; although this situation is somewhat unusual and is apparent only where the isotopic purity of the product is extremely high, e.g., greater than 99.99%, it must always be considered. The isotopic material must also be made homogeneous in solution prior to the final precipitation or other recovery method to ensure that subsequent samples for isotopic analysis and determination of chemical purity will be representative of the entire lot.

Included as part of the purification procedure is the conversion of the isotopic material to a stable chemical form for sales purposes as well as for ultimate scientific use. Hence most of these prepared isotopes are in the form of metals, metal oxides, or reasonably stable salts.

Analysis

After the quantities of various isotopes of a given element have been converted to the desired form, the material, which must approach the quality of both a chemical and an isotopic standard, must be evaluated. In the analysis of standard materials with adequate quantities of sample, multiple determinations are normally used to achieve the desired precision and accuracy. With separated isotopes, however, because of cost and limited availability of material, large samples and replicate determinations are not feasible and, obviously, for the less abundant isotopes, all the recovered isotope might well be needed just for an analysis. Hence what at first glance appears to be no momentous problem becomes a serious economic consideration. For this reason considerable effort has gone into development of analytical as well as purification methods.

CHEMICAL ANALYSIS

The emission spectrograph plays an important part in the chemical analysis of the purified material. Since in most cases the cost of the material limits the determination of the major constituent, i.e., the stable isotope of concern, the alternative is the determination of the impurities and their concentrations; in most applications this is the more accurate method of assessing the concentration of the major constituents. Improvements in analytical procedures, in many instances, have greatly decreased the sample size required to achieve a given level of detection and of precision and accuracy of analysis by spectrochemical methods. The spectrographic method is not, however, without sample cost since all impurities cannot be detected and many cannot be determined accurately under the conditions of a single burn. Furthermore, many of the nonmetallic elements cannot be conveniently determined at all by this method. In some evaluations, neutron activation analysis has been used for the measurement of impurities.

ISOTOPIC ANALYSIS

Isotopic evaluation has been done almost exclusively with mass spectrometry, and Spitzer and Sites[13] have described the method in detail. Sixty-degree deflection, sector type mass spectrometers have been used with conventional ion-focusing and -accelerating slit systems. The analytical sample, in solution or as a slurry, is placed in a trough formed in the center portion of the mounted metal (usually tantalum) ribbon filament. Sometimes two filaments are prepared on the same spectrometer-source base. The solution or slurry on the filament is evaporated to dryness and can be baked under vacuum to fuse a sample or to reduce an oxide. The sample-filament configuration can be used for either thermal or electron-bombardment ionization.

Prevention of isotopic contamination in the preparation of mass spectrometer samples is of extreme importance. The quantity of sample on the filament to be analyzed will range from at most a few milligrams down to a few nanograms. Since the natural abundances of the isotopes of the element to be analyzed have been considerably altered, introduction of even a very small amount of the natural element or of material of different isotopic abundance than that of the element being analyzed can cause drastic errors in the isotopic analysis because of the very small sample size. Thus many steps are taken to eliminate the introduction of impurities. The pipettes for loading the filaments are hand drawn and are discarded after a single use, and new glassware is used for dissolution and preparation of samples. The triply distilled water used is stored in polyethylene bottles to avoid background ions, and the acids and other reagents must be of the highest quality. The filaments must also be free of contamination and are assembled and handled with hemostats, forceps, or tweezers.

Other somewhat less precise methods of isotopic analysis have occasionally been used. Werner et al.[14] applied a hollow cathode and a direct-reading spectrograph for the analysis for lithium isotopes. The technique utilizes the isotopic shift of 0.16 A and is based on measurement of the relative intensities of the characteristic wavelengths of the two isotopes.

Even after isotopic materials have been analyzed, extreme caution must be practiced in their dispensing and handling to prevent chemical and isotopic contamination.

Product Purification Methods

A single method with minor modifications may be suitable for purification of the isotopes of several elements. The purification methods described here include conversion to the inventory form when this differs from that of the final purification step.

DISSOLUTION OF POCKET DEPOSIT

Removal of the deposit from the collectors is, in general, similar for most materials for which the same type of collector, i.e., copper or graphite, is used. Immediately after removal of pockets from the electromagnetic separators, protective tape is placed over openings on both types to prevent entry of foreign materials. The pockets are then scheduled for chemical processing.

When isotope recovery is started, the graphite pockets are carefully cleaned on the outside by buffing with aluminum oxide-coated abrasive cloth. The thick, heavy ends of the pockets are cut off with a hacksaw and discarded; the protective tape is removed; and the pocket is crushed within a plastic bag. The graphite, in a quartz boat, may then be ignited in oxygen at 750 to 800°C in a Vycor tube furnace. Metals and oxides that are highly corrosive to the ignition equipment are processed by removing the bulk (~95%) of the separated isotope from the crushed graphite, prior to ignition, by dissolution in strong nitric acid solution in a large Soxhlet extractor. After the extraction the graphite is removed from the nitric acid solution and ignited to recover the remainder of the material. The ignition ash is dissolved in nitric acid, the solution filtered, and the filtrate combined with the filtered extraction solution.

Copper pockets are carefully cleaned on the outside by washing first with water and then with hot dilute nitric acid. The protective tape is removed, and the deposit is recovered by dissolution in hot dilute nitric acid. In some cases the deposit may be alloyed with the copper; in others it may be buried under a copper film sputtered from adjacent surfaces. Prolonged leaching may be required for difficultly soluble materials, and sometimes the deposit must be undercut with the acid. If the exposed copper surface remains bright after treatment with dilute nitric acid, complete removal of the deposit is usually indicated; if the surface turns dark, alloying material is still present and further leaching is required. Any material not dissolved in the leach solution is filtered, and the residue is digested in acid until dissolution is essentially complete. The filtrate is made to about 20% in nitric acid and electrolyzed with platinum electrodes until all the copper has deposited on the cathode.

STRONTIUM, BARIUM, AND LEAD

The purification of enriched isotopes of these elements is based on the insolubility of the metal nitrate in strong nitric acid.[15,16] A schematic diagram of the purification method is shown in Fig. II-1. Since there are four isotopes each for strontium and lead and seven for barium (Table II-1), the chemical purification procedure must be performed 15 times for the preparation of isotopes of these three elements. Isotopes of these elements may be collected in either graphite or copper receivers. Strontium, barium, and lead are all recovered from graphite pockets by essentially the same method; however, they must be leached from the crushed graphite prior to ignition because they form oxides that are corrosive at the ignition temperature of graphite.

A combination pocket of both copper and graphite has been used for the collection of lead isotopes. A massive graphite pad in the bottom of the pocket provides a striking surface for the energetic ion beam and gives longer collector life. Recovery of material from this type of pocket is similar to that described except that the loose material—lead, copper, and carbon, perhaps combined—is thermally unstable and must be ignited under carefully controlled conditions. The sputtered deposit on the surface is almost insoluble and must be removed by long periods of undercutting with hot concentrated nitric acid.

In the recovery of lead from copper receivers, however, there is one variation as compared with strontium and barium. Lead is deposited quantitatively, under controlled conditions, on the anode as lead dioxide during the electrolysis for removal of copper and is collected by dissolution of this deposit at room temperature in 1:4 nitric acid with frequent additions of small quantities of 30% hydrogen peroxide. When the bulk of the deposit has dissolved, the solution can be warmed.

For the precipitation steps in the purification of strontium, barium, or lead, the nitrate solution (filtered where necessary) recovered from

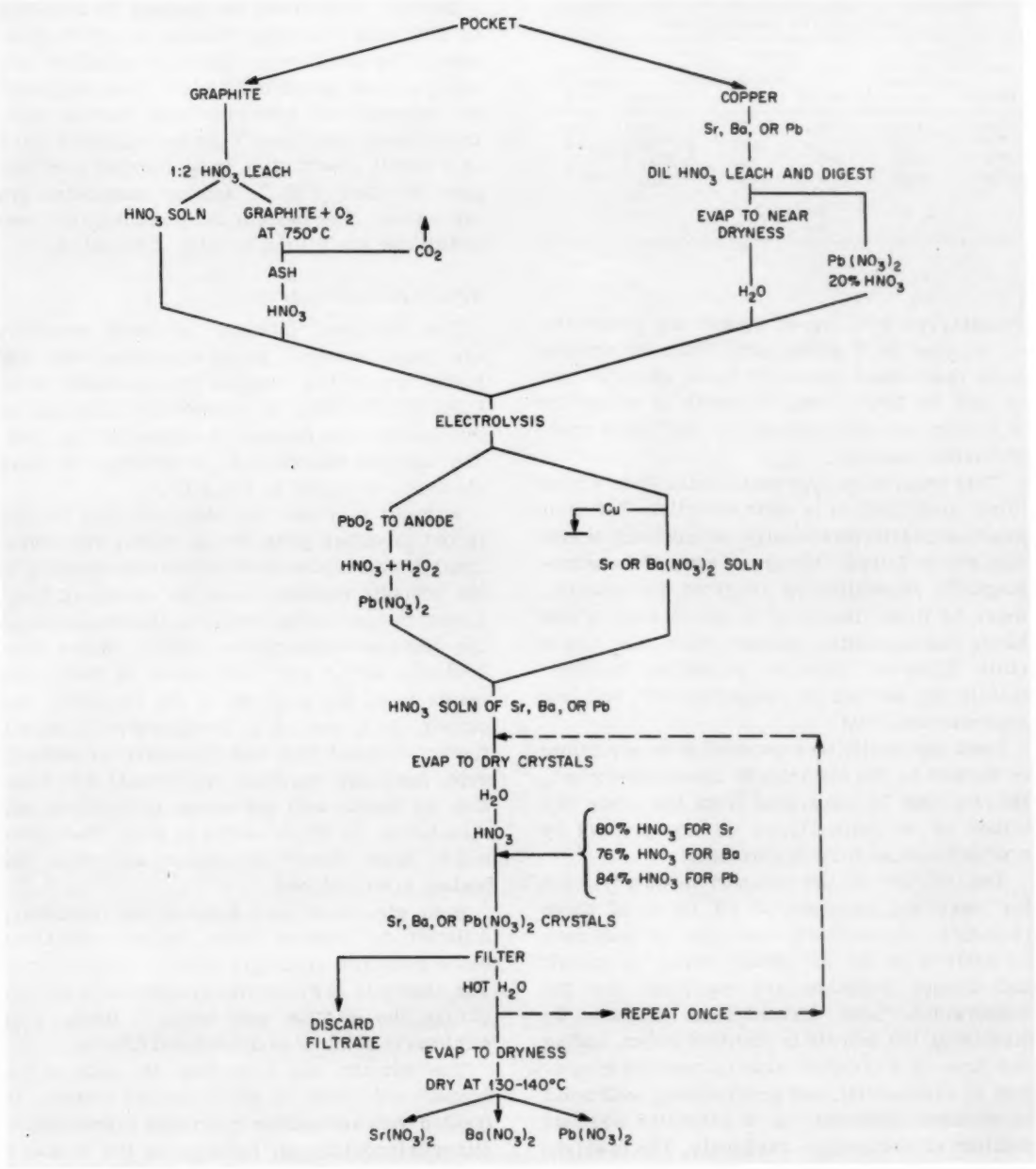


Fig. II-1 Purification method for enriched isotopes of strontium, barium, or lead.

either the electrolysis solution from the copper or graphite pockets or the solution obtained by dissolving the PbO_2 from the anode is evaporated to a dry crystalline deposit of the nitrate. The crystals are dissolved in a known, small amount of water, and fuming nitric acid is added to bring the HNO_3 concentration (by weight) to 80% for strontium, 76% for barium, or 84% for lead. The crystals of nitrate are allowed to settle for about 30 min, and then they are vacuum filtered. The residue is redissolved with water, evaporated to dryness, and then reprecipitated and filtered. The crystals are again dissolved in water, and the solution is

Table II-1 NATURAL ABUNDANCES OF STRONTIUM, BARIUM, AND LEAD ISOTOPES

Strontium		Barium		Lead	
Isotope	Abundance, at.%	Isotope	Abundance, at.%	Isotope	Abundance, at.%
^{84}Sr	0.56	^{130}Ba	0.101	^{204}Pb	1.48
^{86}Sr	9.86	^{132}Ba	0.097	^{206}Pb	23.6
^{87}Sr	7.02	^{134}Ba	2.42	^{207}Pb	22.6
^{88}Sr	82.56	^{135}Ba	6.59	^{208}Pb	52.3
		^{136}Ba	7.81		
		^{137}Ba	11.32		
		^{138}Ba	71.66		

transferred to a Pyrex beaker and evaporated to dryness on a steam bath. When the crystals have been dried overnight in an electric oven at 135 to 140°C, the material is ready for sampling for spectrochemical and mass spectrometric analysis.

This separation by crystallization from strong nitric acid solution is quite selective. The main sources of interference are the elements within this group. Unless introduced after the electromagnetic separation by reagents, for example, there is little likelihood of one element of this group contaminating another since they are of quite different masses: strontium approximately 88, barium approximately 138, and lead approximately 208.

Lead can easily be separated from strontium or barium by the electrolytic method described. Barium can be separated from the other two either as an impurity or as the product by precipitation as barium chromate.

The nitrate is the common inventory form for enriched isotopes of all three of these elements. Occasionally isotopes of lead may be desired as the carbonate, oxide, or metal, and simple methods are employed for the conversions. Lead carbonate is produced by dissolving the nitrate in distilled water, adding one drop of 1:1 nitric acid (to prevent formation of basic salts), and precipitating with solid ammonium carbonate or a saturated aqueous solution of ammonium carbonate. The precipitate is washed with water, then acetone, and dried at 100 to 110°C.

Lead oxide, PbO, is formed by ignition of either the nitrate or carbonate in platinum. The carbonate is preferred because the nitrate crystals tend to decrepitate at approximately 470°C and losses are higher. The carbonate usually is ignited at 650°C, and the Pb_3O_4 that is formed during ignition is quantitatively converted[17] to PbO at 610 to 619°C.

Isotopic lead metal is obtained by reduction of PbO with hydrogen, carbon, or carbon monoxide. The simplest procedure is with hydrogen, using a small graphite crucible (even hollowed-out commercial spectrographic carbon electrodes have been used[18]). Reduction takes place in a small quartz tube in an electric tube furnace at about 600°C, and no impurities are introduced. The bead or button of metallic lead is suitable for rolling or other fabrication.

ZIRCONIUM AND HAFNIUM

The enriched isotopes of these elements are purified[19,20] by precipitation with the highly specific reagent DL-mandelic acid, $C_6H_5CH(OH)COOH$. A schematic diagram of the purification method is shown in Fig. II-2. The natural abundances of isotopes of these elements are given in Table II-2.

Isotopes of these two elements may be collected in either graphite or copper receivers. Ignition can immediately follow the crushing of the graphite pockets since the oxides of these elements are not corrosive to the equipment at the ignition temperature, 800°C; thus a preliminary nitric acid extraction of these elements from the graphite is not required. The oxides, ZrO_2 and HfO_2, are dissolved, respectively, with hot 60% and concentrated sulfuric acid. Insoluble residues are brought into solution by fusion with potassium pyrosulfate and dissolution in dilute sulfuric acid. The solutions, from direct dissolution and from the fusion, are combined.

Both zirconium and hafnium are relatively difficult to remove from copper collectors since both are sparingly soluble in nitric acid. The elements are removed by essentially undercutting the deposit with hot 1:1 HNO_3. This nitric acid solution is diluted and filtered.

The filtrate, which contains the bulk of the copper and little of the collected isotope, is treated with ammonium hydroxide to precipitate either zirconium or hafnium as the hydrated oxide, i.e., $ZrO_2 \cdot 2H_2O$ or $HfO_2 \cdot 2H_2O$. This precipitate is filtered and dissolved in nitric acid solution, and any copper present is removed by electrolysis.

The residue from the initial filtration, which contains the bulk of the separated isotope of zirconium or hafnium as metal, is dissolved in a mixture of nitric and sulfuric acids. Continued digestion with hot concentrated sulfuric acid is required to bring all the hafnium into

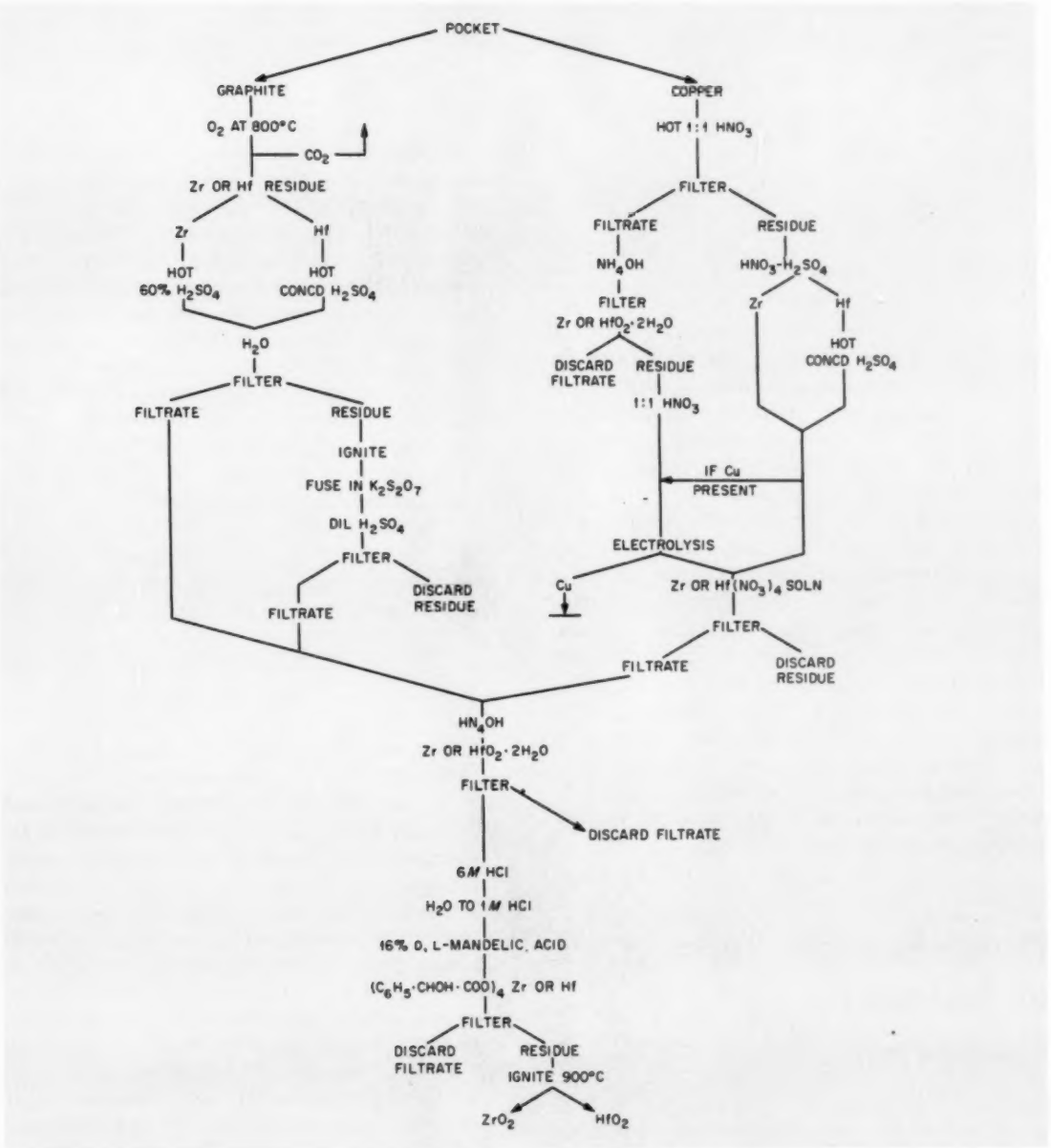


Fig. II-2 Purification method for enriched isotopes of zirconium or hafnium.

solution. If any appreciable amount of copper is present, it may be removed by electrolysis. This solution is combined with that from the initial filtrate.

The acid solution of the isotope recovered from either the graphite or the copper receiver is treated with ammonium hydroxide to precipitate the hydrated oxide. Care is taken not to digest this precipitate on a steam bath or to allow it to become hot, since heating produces an oxide of lower water content which is difficultly soluble even in strong acids.

The hydrated oxide is dissolved with 6*M* HCl, and the solution is adjusted to 1*M*. A 16% solution of DL-mandelic acid (150 ml per gram of oxide) is added to precipitate the zirconium or

Table II-2 NATURAL ABUNDANCES OF ZIRCONIUM AND HAFNIUM ISOTOPES

Zirconium		Hafnium	
Isotope	Abundance, at.%	Isotope	Abundance, at.%
^{90}Zr	51.46	^{174}Hf	0.18
^{91}Zr	11.23	^{176}Hf	5.20
^{92}Zr	17.11	^{177}Hf	18.50
^{94}Zr	17.40	^{178}Hf	27.14
^{96}Zr	2.80	^{179}Hf	13.75
		^{180}Hf	35.24

hafnium. The precipitate is digested 30 min at 85°C, and, after filtration, the residue is ignited first at approximately 300°C and then at 900°C. The dioxide produced upon ignition, ZrO_2 or HfO_2, is the stable inventory form and is used for the subsequent spectrographic and mass spectrometric analyses.

Precipitation with DL-mandelic acid is quite selective for these two elements; the main source of interference is, of course, the other element in the group. Kumins[19] found no interferences from aluminum, antimony, barium, bismuth, cadmium, calcium, cerium, chromium, copper, iron, thorium, tin, titanium, or vanadium. The effect of cobalt, magnesium, manganese, mercury, nickel, uranium, and zinc on the method was investigated by Hahn,[20] who found that successful separations of these elements from zirconium and hafnium can be made with DL-mandelic acid.

(R. E. Greene and P. S. Baker)

Photochemical Separation of Isotopes*

By Jean Rozenbergt

A review of the literature on photochemical separation of mercury isotopes indicates this to be a promising technique. Good separation requires that the isotope bands in the absorption spectrum of the element be widely separated and that the product enriched by photoselective reaction not be contaminated by secondary reactions. Separation of mercury isotopes is a well-developed procedure and is about to become industrial. Lithium isotopes should theoretically be separable by such a technique, but handling of molten lithium is difficult. The failure of the first attempts to separate chlorine and uranium isotopes is probably due to misjudgment of the primary mechanisms and to the use of too simple techniques. Hydrogen isotopes may be separated with light sources with H (or D) α Lyman sources, but yields are too low for large-scale use.

In 1920, Merton and Hartley[21] tried to synthesize HCl in a mixture of hydrogen and chlorine gases where only the mass 37 isotope was photoexcited. This first attempt to use a selective excitation process to separate a particular isotope failed, and, as a result, photochemical separation has remained in the domain of laboratory research. In order to define the method and the conditions necessary for obtaining photochemical separation, the separations of isotopes of various elements that have been studied were reviewed.

The principle of the method is simple: If a single isotope, A_1, of an element that is made up of a mixture of several isotopes can be excited by absorption of a sufficiently narrow spectral band and made to enter into photochemical reactions such as

$$A_1 + B \rightarrow A_1B$$

$$A_1B \rightarrow A_1 + B$$

the products that contain only isotope A_1 may be isolated from the reaction. For the excitation to be selective, the isotope bands in the absorption spectrum of the element should be widely separated. Such separations in the atomic and molecular spectrums are due chiefly to differences in the isotope masses, the existence of molecular spins, and differences in nuclide volumes. Gibert[22] investigated the possibilities offered by molecular spectrums and indicated the possibility of using vibration–rotation spectrums for selectively increasing the vibration energy of an isotopic molecular species.

We should be able to use an intense source of light with a sufficiently narrow spectral band to excite only one isotopic species. It would be necessary to prevent widening of the band by the Doppler effect by working at low temperatures and to prevent collision reactions by working at low pressures. It should also be possible to use the inverse method, which consists in filtering out a very narrow band from a wide band so that all the isotopes except the one studied contribute to the absorption.

The problem of choice of reagents entering into a photochemical reaction with selectively excited atoms and not with the others is basic.

*CEA-BIB-56, May 1965 [in French; ORNL-tr-1045 by Martha Gerrard (edited)].

†Centre d'Etudes Nucleaires, Saclay, France.

The separation can be really effective only if secondary reactions between the product and the original reaction mixture are suppressed.

Mercury

Mercury, whose natural isotopic composition is shown in Table II-3, is especially suitable for a photochemical method of separation. The 2537-A band has a hyperfine structure due to nuclear spins. If natural mercury is irradiated with a lamp that contains one of the pure isotopes, the isotope can be selectively excited from the 6^1S_0 state to the 6^3P_1.

Table II-3 ISOTOPIC COMPOSITION OF NATURAL MERCURY

Atomic mass	Abundance, %	Atomic mass	Abundance, %
196	0.16	201	13.22
198	10.02	202	29.72
199	16.92	204	6.84
200	23.10		

Zuber[23–25] used a Mozrowski filter in an attempt to separate the 200 and 202 isotopes of mercury by selective oxidation. He observed an isotopic enrichment in the recovered mercury oxide when the oxidant was pure air and the total absence of enrichment with pure oxygen.

In 1952, McDonald and Gunning[26] studied the reaction of air with mercury excited by a discharge in ^{198}Hg. At 150°C, as a result of the widening and the self-absorption of the excited band, the mercury oxide formed did not contain the 198 isotope but, on the contrary, was enriched in some other isotopes (Table II-4).

Table II-4 ISOTOPIC COMPOSITION OF MERCURY OXIDE OBTAINED BY PHOTOSENSITIZED REACTION AT ELEVATED PRESSURE

Isotope	Abundance, %	Isotope	Abundance, %
198	0.158	201	24.62
199	10.71	202	14.34
200	18.17	204	31.99

Robinson, Carpenter, and Wilson[27] obtained mercury slightly enriched in the 198 isotope.

In 1953, Billings, Hitchcock, and Zelikoff[28] succeeded in enriching the 198 isotope in the mercury oxide formed in water vapor in the presence of nitrogen. For the first time an electrodeless discharge was used. In a similar study[29] with a ^{202}Hg source, enrichments in ^{202}Hg were observed.

The enrichment factor ($f = 1.5$) obtained by Billings was the subject of a patent.[30] About the same time the Russians told about a similar study.[31]

In 1957, Osborn, McDonald, and Gunning[32] obtained a significant increase in the isotopic enrichment of ^{202}Hg by addition of butadiene, the oxidant being water vapor; in 1958, Gunning[33] published results of experiments on enrichment with various oxidizing and chlorinating agents. Of the three oxidants used—water vapor, nitrous oxide, and oxygen—only the water vapor gave an isotopic enrichment in the mercury oxide under the effect of the light from electrodeless lamps with ^{198}Hg and ^{202}Hg.

The formation of enriched calomel has also been studied.[34–39] The reagents used were HCl, methyl chloride, methylene chloride, chloroform, CCl_4, isopropyl chloride, and boron trichloride. There was no enrichment in CCl_4 or BCl_3, and the addition of butadiene increased the enrichment only with HCl. The calomel residue was recovered by dissolution in concentrated HCl, and the mercury was fixed on copper or gold. The isotopic composition was determined by absorptiometry of the resonance bands.

In 1960, Sherwood and Gunning,[40] in polymerizing acetylene photosensitized with mercury, recovered mercury highly enriched in ^{202}Hg, 82.3% compared to the natural abundance of 29.7%.

More recently, experimental techniques have been improved, especially by measuring the enriched calomel yields by mass spectrometry. Mercury depletion in the container is measured, and intermittent illumination by lamps with electrodeless discharge is used. Poole[41] and Gunning,[42] who used HCl, established the fact that enrichment in the 198 and 201 isotopes increases with increasing flow rate and concentration of butadiene and with use of intermittent illumination; it decreases when the lamp temperature is increased. With alkyl and vinyl chlorides, Wan,[43] using a ^{202}Hg lamp, obtained similar results except that butadiene was not used. Tables II-5 and II-6 give these results plus those of Dingle,[44] who studied separa-

Table II-5 MAXIMUM ENRICHMENT IN MERCURY VAPOR[41-43] BY PHOTOEXCITATION IN HCl

Isotope	Natural abundance, %	Isotopic abundance in recovered calomel, %			
		Continuous illumination		Intermittent illumination	
		Pure HCl	30% C_4H_6	Pure HCl	30% C_4H_6
198	10.02	14.1	30.6	22.2	33.2
201	13.22	14.8	19.0	15.6	17.9
202	29.72	36.0	-	45.2	-

Table II-6 MAXIMUM ENRICHMENT OF ^{202}Hg IN MERCURY VAPOR[43,44] BY PHOTOEXCITATION IN ALKYL AND VINYL CHLORIDES

Compound	Abundance, %		Compound	Abundance, %	
	Continuous illumination	Intermittent illumination		Continuous illumination	Intermittent illumination
CH_3Cl	37	50	CF_3Cl	-	31
C_2H_5Cl	38	53	CF_2Cl_2	-	31
C_3H_7Cl	-	54	$CFCl_3$	-	30
$i\text{-}C_3H_7Cl$	43	52	CF_2HCl	-	39
$i\text{-}C_4H_9Cl$	36	48	$CFHCl_2$	-	33
$C_5H_{11}Cl$	-	54	CH_3CF_2Cl	-	34
C_2H_3Cl	44	52	CH_3CH_2Cl	-	51
CH_3Cl	-	51	CH_3CHCl_2	-	48
CH_2Cl_2	-	50	CH_3CCl_3	-	32
$CHCl_3$	-	44	CH_2ClCH_2Cl	-	43
CCl_4	-	31	$CH_2ClCHCl_2$	-	50

tion in alkyl chlorides, some of which were fluorinated.

Desnoyer, Nief, and Roth[45] reexamined the oxidation of mercury vapor by mixtures of water vapor, oxygen, and butadiene. They showed that two oxidation mechanisms go on at the same time. One is isotopically selective, but the other, blocked by butadiene, is not. They note that oxygen is more effective than water but less than the mixture of the two, and they conclude that the first step in the reaction is formation of an excited associated state between the mercury vapor and the oxygen of water. The second step is a rupture of this structure and leads to the formation of either HgO, which is the isotopic oxidation, or metallic mercury. The other fragments, which contain the oxidant species, produce the ordinary oxidation of mercury. Butadiene blocks this oxidation without affecting the isotopic oxidation. This method has given mercury in which the 202 isotope occurs in 95% abundance.

An apparatus used in photochemical separation of mercury isotopes is shown in Fig. II-3.

A program for the photochemical separation of ^{204}Hg has been initiated,[46] and a price of $95 for a kilogram of ^{204}Hg is visualized for a total production[47] of 2500 kg.

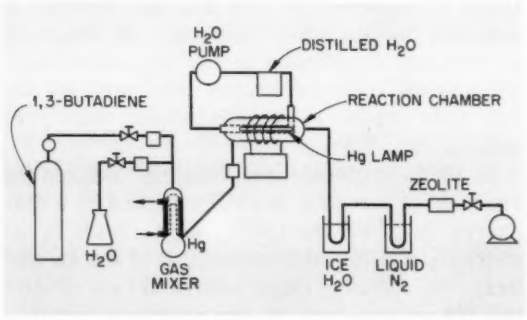


Fig. II-3 Mercury-isotope separator.

Lithium

The lithium resonance band at 6708 A is a doublet that has a hyperfine structure due to the isotopic effect, and the intensities of the lines are essentially proportional to the isotopic abundances. This fact indicates a theoretical enrichment much better than for mercury. However, handling of molten lithium is a very difficult engineering problem, and, to our knowledge, there have not yet been any experimental studies on photochemical separation of lithium isotopes. Two preliminary studies[27,48]

have been made to determine the possibilities of such a separation.

Chlorine

Since the first attempt of Merton and Hartley[21] only Kuhn and Martin have tried to separate chlorine isotopes by a photochemical method. In 1922, Hartley et al.[49] irradiated a mixture of chlorine and hydrogen with white light filtered by natural chlorine but found no separation of ^{37}Cl. We know today that, under these experimental conditions, chain reactions are initiated which involve both ^{37}Cl and ^{35}Cl. Later, a slight excess of ^{35}Cl was obtained[50,51] in the chlorine liberated by photolysis of phosgene.

Kuhn, Martin, and Eldau[52] tried to use the fortuitous coincidence of the mercury bands at 3663 and 3654 A with the absorption bands of the $^{35}ClO_2$ and $^{37}ClO_2$ molecules to enrich the chlorine in the 35 isotope. They found an increase in the $^{35}Cl/^{37}Cl$ ratio from 3.41 to 5.57, but the result seems to be coincidental and could not be extrapolated to a general case.

Uranium

Although the emission from a mixture of uranium isotopes has a hyperfine structure, Urey[53] and Diecke[54] were unsuccessful in attempts to separate ^{235}U photochemically.

An enrichment in ^{235}U should be obtainable by a process similar to photochemical effects.[55] It consists in vaporizing or condensing an element in an isotopic mixture in the presence of a solid body that is hotter and emits a selectively absorbed infrared band.

Hydrogen

The work of Tanaka, McNesby, and Koyano,[56,57] who studied the photosensitizing reaction between H or D atoms in their ^2P state and molecular nitrogen, warrants special examination in order to determine whether it can be applied to photochemical separation of hydrogen isotopes. The discharge of ultrashort waves in a stream of hydrogen produces H (^2S) atoms. They are put into the ^2P state by the H α Lyman radiation at 1216 A. These atoms react with the molecular nitrogen to give light ammonia. With a light source with a D α Lyman radiation and a stream of molecular deuterium similarly excited, heavy ammonia is obtained. On the other hand, a mixture of $H_2 + H + N_2$ (I) excited by a D α Lyman source and a mixture of $D_2 + D + N_2$ (II) excited by an H α Lyman source do not produce ammonia.

These results show the selective effect of light sources, but large-scale production of heavy ammonia from natural hydrogen does not seem practicable. The authors have some reservations concerning the absence of light ammonia in system I. Even if this absence should be confirmed, their maximum production was 1.44×10^{-9} gram molecule of ND_3 (2.16×10^{-9} gram molecule of D_2) per second in pure deuterium. In natural hydrogen, which contains about 110 ppm deuterium, we would obtain

$$2.16 \times 10^{-9} \times 10^{-4} \times 3.6 \times 10^{3} \times 24 \times 365 = 6.8 \times 10^{-6} \text{ gram molecule of } D_2$$

after a year of continuous operation of a single lamp.

References

The Chemistry of Electromagnetically Separated Stable Isotopes

1. Stable Isotopes, *Isotopes Radiation Technol.*, 1(1): 43-52 (Fall 1963).
2. B. Weaver, Chemical Refinement Procedures in the Electromagnetic Separation of Isotopes, USAEC Report ORNL-1952, Oak Ridge National Laboratory, Apr. 8, 1955.
3. M. L. Smith, Electromagnetic Enrichment of Stable Isotopes, in *Progress in Nuclear Physics*, Vol. 6, pp. 180-183, O. R. Frisch (Ed.), Pergamon Press, New York, 1957.
4. P. S. Baker, A Fifteen-Year Summary of Publications Involving the Uses of Electromagnetically Enriched Stable Isotopes, USAEC Report ORNL-3266, Oak Ridge National Laboratory, Apr. 4, 1963.
5. B. Weaver, Preparation of Charge Materials for Electromagnetic Isotope Separation, in *Electromagnetically Enriched Isotopes and Mass Spectrometry*, pp. 82-96, M. L. Smith (Ed.), Conference Proceedings, Harwell, 1955, Academic Press Inc., New York, 1956.
6. C. W. Sheridan, H. R. Gwinn, and L. O. Love, Preparation of Charge Materials for ORNL Electromagnetic Isotope Separators, USAEC Report ORNL-3301, Oak Ridge National Laboratory, Aug. 2, 1962.
7. *Ibid.*, pp. 5-7.
8. B. J. Sturm and C. W. Sheridan, Vanadium (III) Fluoride, in *Inorganic Syntheses*, Vol. VII, pp. 87-92, Jacob Kleinberg (Ed.), McGraw-Hill Book Company, Inc., New York, 1963.
9. P. S. Baker, Stable Isotopes: Aid to Research, *Chem. Eng. News*, 37: 60-65 (Feb. 2, 1959).
10. T. C. Rains, H. E. Zittel, and Marion Ferguson, Flame Spectrophotometric Determination of Mi-

cro Concentrations of Strontium in Calcareous Material, *Anal. Chem.*, 34: 778-781 (1962).
11. V. C. Farmer, Spectrographic Investigations on the Minor-Element Content of Plants and Soils, Thesis, University of Aberdeen, Scotland, unpublished, 1946.
12. R. L. Mitchell, *The Spectrographic Analysis of Soils, Plants, and Related Materials*, Technical Communication No. 44, pp. 129-130, Commonwealth Bureau of Soil Science, Harpenden, England, 1948.
13. E. J. Spitzer and J. R. Sites (Comps.), Isotopic Mass Spectrometry of the Elements, USAEC Report ORNL-3528, Oak Ridge National Laboratory, Dec. 17, 1963.
14. G. K. Werner, D. D. Smith, S. J. Ovenshine, O. B. Rudolph, and J. R. McNally, Jr., Further Investigations in the Spectro-Isotopic Assay Technique for Lithium, *J. Opt. Soc. Am.*, 45: 202-205 (March 1955).
15. H. H. Willard and E. W. Goodspeed, Separation of Strontium, Barium, and Lead from Calcium and Other Metals, *Anal. Chem.*, 8: 414-418 (1936).
16. W. C. Davis, F. B. Thomas, R. L. Bailey, F. M. Scheitlin, and P. S. Baker, Purification of Salts by Precipitation with Concentrated Nitric Acid, (Abs.), *J. Tenn. Acad. Sci.*, 32: 127 (1957).
17. C. Duval, *Inorganic Thermogravimetric Analysis*, translated by R. E. Oesper from the French manuscript, p. 621, American Elsevier Publishing Company, Inc., New York, 1963.
18. P. S. Baker, A Rapid Efficient Method for Reducing Certain Metallic Isotopic Oxides, *J. Chem. Ed.*, 38: 117 (March 1961).
19. C. A. Kumins, Zirconium Determination in Presence of Interfering Elements, *Anal. Chem.*, 19: 376-377 (1947).
20. R. B. Hahn, Determination of Small Amounts of Zirconium with Mandelic Acid, *Anal. Chem.*, 21: 1579-1580 (1949).

Photochemical Separation of Isotopes

References marked with an asterisk were not checked by the translator.

21. T. R. Merton and H. Hartley, The Separation of Isotopes, *Nature*, 105: 104-105 (1920).
22. R. Gibert, Conditions for Possible Isotope Enrichment by a Photochemical Reaction (in French), *J. Chim. Phys.*, 60: 205-208 (1963).
23. K. Zuber, Study of the Separation of Hg Isotopes (in German), *Helv. Phys. Acta*, 8: 488-490 (1935).
24. K. Zuber, Separation of the Hg Isotopes by a Photochemical Method, *Nature*, 136: 796 (1935).
25. K. Zuber, Separation of Hg Isotopes by a Photochemical Method (in German), *Helv. Phys. Acta*, 9: 285-300 (1936).
26. C. C. McDonald and H. E. Gunning, Isotope Enrichment by the Photoexcitation of Specific Isotopes, *J. Chem. Phys.*, 20: 1817 (1952).
27. D. Z. Robinson, R. O. B. Carpenter, and M. K. Wilson, Photochemical Separation of Isotopes. Progress Report Covering the Period April 1, 1952 to June 30, 1952, Report JO-5076, Baird Associates, Inc., Aug. 29, 1952 (USAEC file No. NP-4834).
28. B. H. Billings, W. J. Hitchcock, and M. Zelikoff, The Photochemical Separation of Isotopes, *J. Chem. Phys.*, 21: 1762-1766 (1953).
29. M. Zelikoff, L. M. Aschenbrand, and P. H. Wyckoff, Photochemical Enrichment of ^{202}Hg, *J. Chem. Phys.*, 21: 376 (1953).
30. B. H. Billings, Photochemical Isotope Separation, U. S. Patent No. 2,713,025, 1955 (*Chem. Abstr.*, 49: 13790c).
31. I. P. Shmelev, A Photochemical Method for Separating Mercury Isotopes (in Russian), *Priroda*, 1955, No. 1: 84-85 (English translation JPRS-2393).
32. K. R. Osborn, C. C. McDonald, and H. E. Gunning, Photochemical Separation of Hg Isotopes. I. A Study of the Emission and Absorption Hyperfine Lines of Hg at 2537 A, *J. Chem. Phys.*, 26: 124-133 (1957).
33. H. E. Gunning, Primary Processes in Reactions Initiated by Photoexcited Hg Isotopes, *Can. J. Chem.*, 36: 89-95 (1958).
34. R. Pertel and H. E. Gunning, Photochemical Separation of Hg Isotopes. II. The Reaction of ^{202}Hg $6(^3P_1)$ Atoms, Photoexcited in Natural Hg Vapor, with Water Vapor and Other HgO-forming Substrates, *Can. J. Chem.*, 37: 35-42 (1959).
35. C. C. McDonald, J. R. McDowell, and H. E. Gunning, Photochemical Separation of Hg Isotopes. III. The Reaction of ^{202}Hg $6(^3P_1)$ Atoms, Photoexcited in Natural Hg Vapor, with Hydrogen Chloride, *Can. J. Chem.*, 37: 930-939 (1959).
36. K. R. Osborn and H. E. Gunning, Photochemical Separation of Hg Isotopes. IV. The Reaction of ^{202}Hg $6(^3P_1)$ Atoms, Photoexcited in Natural Hg Vapor, with Methyl Chloride and Isopropyl Chloride, *Can. J. Chem.*, 37: 1315-1327 (1959).
37. J. R. McDowell, C. C. McDonald, and H. E. Gunning, Photochemical Separation of Hg Isotopes. V. Further Studies on the Reaction of ^{202}Hg $6(^3P_1)$, Photoexcited in Natural Hg Vapor, with Hydrogen Chloride, *Can. J. Chem.*, 37: 1432-1441 (1959).
38. R. E. Ewing, Photochemical Separation of Mercury Isotopes, USAEC Report HW-63177, Hanford Atomic Products Operation, Dec. 23, 1959.
39. E. E. Voiland, Separation of Mercury Isotopes by Selective Photoexcitation, USAEC Report HW-59329, Hanford Atomic Products Operation, Mar. 5, 1959.
40. A. G. Sherwood and H. E. Gunning, The Primary Process in the Hg-$6(^3P_1)$-Photosensitized Polymerization of Acetylene, *Can. J. Chem.*, 38: 466-467 (1960).
41.*J. A. Poole, Thesis, University of Alberta, 1961.
42. H. E. Gunning, The Photochemical Separation of Hg Isotopes, *J. Chim. Phys.*, 60: 197-204 (1963).
43.*J. K. S. Wan, Thesis, University of Alberta, 1962.
44. T. Dingle and H. E. Gunning, unpublished data, cited by H. E. Gunning and O. P. Strausz, Isotopic Effects and the Mechanism of Energy Transfer in Hg Photosensitization, in *Advances in Photochemistry*, Vol. 1, pp. 209-274 (especially p. 219), Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1963.
45. M. Desnoyer, G. Nief, and E. Roth, Photochemical Oxidation of Hg and Isotope Selectivity (in French), *J. Chim. Phys.*, 60: 209-211 (1963).
46. D. B. Cooper and N. P. Otto, Mercury-204 Photochemical Separation Program. Phase 1, Final Report, USAEC Report TID-11024, Thompson Ramo Wooldridge Inc., Aug. 29, 1960.
47. C. A. Rohrmann, Estimated Costs for the Production of Pure Mercury-204 Isotope, USAEC

Report HW-71793, Hanford Atomic Products Operation, Dec. 1, 1961.

48. L. M. Dorfman, Isotope Separation by the Photoexcitation of Specific Isotopes: The Possibility of Applying This Method to the Separation of ^{6}Li and ^{7}Li, USAEC Report KAPL-M-LMD-2, Knolls Atomic Power Laboratory, Nov. 28, 1952.
49. H. Hartley, A. O. Ponder, E. J. Bowen, and T. R. Merton, An Attempt To Separate the Isotopes of Chlorine, *Phil. Mag.*, 43: 430-435 (1922).
50. M. Hartmann, M. Laue, C. Neuberg, A. Rosenheim, and M. Volmer, Photochemical Separation of Isotopes (in German), *Naturwissenschaften*, 20: 772 (1932).
51. W. Kuhn and H. Martin, Photochemical Separation of Isotopes (in German), *Z. Physik. Chem. (Leipzig)*, 21B: 95-137 (1933).
52. W. Kuhn, H. Martin, and K. H. Eldau, Enrichment of Chlorine Isotopes by Irradiation of Chlorine Dioxide at Low Pressure (in German), *Z. Physik. Chem. (Leipzig)*, 50B: 213-254 (1941).
53. H. C. Urey, Investigation of the Photochemical Method for Uranium Isotope Separation, USAEC Report A-750, Columbia University, July 10, 1943.
54. G. H. Diecke, The Uranium Isotope Effect and Other Features in the Absorption and Fluorescence Spectra of Uranyl Chloride, USAEC Report A-3227, Johns Hopkins University, Mar. 23, 1945.
55. *British Patent No. 836,857, 1958.
56. I. Tanaka and J. R. McNesby, Photosensitized Reaction Between H (^{2}P) Atoms and Molecular Nitrogen, *J. Chem. Phys.*, 36: 3170-3173 (1962).
57. *I. Koyano and I. Tanaka, *J. Chem. Phys.*, 60: 205 (1964).

Section

III

Isotopes and Radiation Technology

Isotope Technology Development

The preparation and properties of Kryptonates, new materials in which ^{85}Kr is incorporated in a wide variety of solids for many uses, are summarized in this issue. The use of Kryptonates in analytical chemistry is stressed.

Another important phase of radioisotope technology, instrumentation based on use of radioisotopes, is also reviewed. An abridged form of the Rotariu paper, which reviewed U. S. development in this field at the symposium on Radioisotope Instruments in Industry and Geophysics in October 1965, in Warsaw, Poland, is given together with a summary of the entire symposium.

Readers of this section are also directed to Sec. VI, which contains a paper by P.-E. E. Bergner. This paper, a review of the theoretical basis of tracer technology in biomedical research, should also find application in industrial and geophysical uses.

Preparation, Properties, and Uses of Kryptonates in Chemical Analyses

Krypton-85 has been stably incorporated into a wide variety of solids. These solid sources, termed "Kryptonates," have been prepared by bombardment of solids with ionized krypton and by diffusion of krypton into solids at high temperature and pressure. Sources prepared by either method display essentially the same useful and unique properties. They are stable over extended periods of time at room temperature, and they are remarkably stable at elevated temperatures. The Kryptonates are sensitive to chemical disturbances at the surface, and such disturbances lead to proportional losses of ^{85}Kr. This property is the basis of the use of Kryptonates in chemical analyses.

Krypton-85 is a radioisotope that has the advantages of a useful half-life (10.7 years), an almost pure beta emission (0.695 Mev), and a chemical inertness, but also the disadvantage of being difficult to use because of its lack of reactivity. A new method of handling ^{85}Kr so that it became a useful source of beta radiation was provided by the development, by Chleck and coworkers, of radioactive clathrates. This research was reviewed in the first issue of *Isotopes and Radiation Technology*.[1] The production of radioactive clathrates, as well as work on radiochemical exchange techniques,[2] was a stepping stone to the development of techniques for the utilization of ^{85}Kr as a universal tracer.

Krypton-85 is called the "universal tracer" because, by methods developed primarily by Chleck, Cucchiara, and coworkers at Parametrics, Inc., and supported by the U. S. Atomic Energy Commission's (AEC) Division of Isotopes Development (DID) and the U. S. Air Force, this one radioisotope can be used as a tracer in at least 125 solids. The ^{85}Kr is released for counting when the solids that have been impregnated with the ^{85}Kr react with the chemical or physical environment. The loss of ^{85}Kr can then be used to detect and measure the effect. These unique solid sources, termed "Kryptonates,"* have potential application in a wide variety of areas. In a past issue of *Isotopes and Radiation Technology*,[3] a brief discussion of Kryptonates was included by Fowler and Aebersold in their summary of the status of AEC's research and developmental activities.

In the discussion that follows, a review of the applications of Kryptonates in analytical chemistry is preceded by a consideration of the preparation and properties of Kryptonates. Applications of Kryptonates in materials research will be reviewed in a subsequent issue.

*Trademark of Parametrics, Inc., and not to be confused, for example, with the salt produced when krypton tetrafluoride reacts with an aqueous alkali solution.[4]

Preparation and Properties of the Kryptonates

PREPARATION

The Kryptonates are prepared by two general methods:

1. The ion-bombardment method, in which the krypton atoms are ionized and impelled into a solid. In addition to standardizing the electron- and ion-bombardment conditions, Chleck, Maehl, and Cucchiara[5] and Goodman and Ronayne[6] concur in the importance of standardizing pre-bombardment etching of the solid (target) and degassing of the apparatus. Chleck's final technique,[5] which yielded reproducible samples, begins with an etching of the solid for 3 sec in a mixture of sulfuric, nitric, and hydrofluoric acids. The etched solid is placed in the ion-bombardment apparatus (Fig. III-1), which is

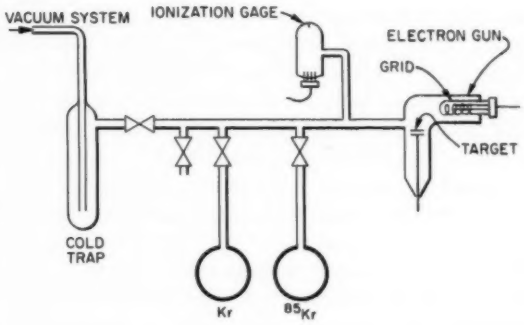


Fig. III-1 Ion-bombardment apparatus.

operated under reduced pressure attained by a combination of forepump and oil-diffusion pump. External heating of the electron gun aids in the degassing of the bombardment apparatus. A small volume of gas containing approximately 5% ^{85}Kr in krypton* is introduced to the bombardment system and ionized by the electron emitter (filament of the electron gun). Under a high negative potential, this plasma of ionized gases is impelled into the target.

2. The diffusion method, in which krypton atoms at high pressure and temperature diffuse into the solid. The solid is placed in a pressure bomb (Fig. III-2), and ^{85}Kr is introduced at low temperature and pressure. The bomb is then closed off from the remainder of the system, and pressure is raised by heating the bomb with an oil bath, heating tape, or furnace. The pressure is controlled by regulating the volume of gas introduced and the temperature of the bomb.

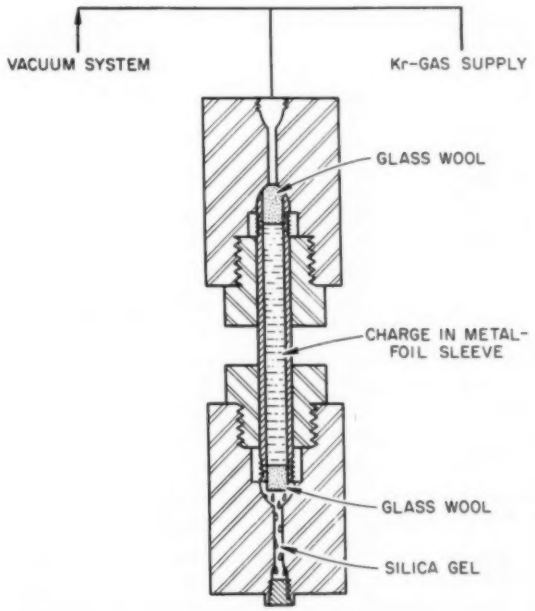


Fig. III-2 Pressure bomb and connections of the high-pressure high-temperature diffusion apparatus.
Fig. III-3 Krypton gas collected as a function of (a) time, (b) pressure, and (c) temperature.

Temperature measurements may be based on bomb temperatures or calculated from the measured pressures by using the ideal-gas equation and published values for the deviations of krypton from ideality. At the completion of a run, the material is quenched by immersing the pressure bomb in liquid nitrogen. The amount of krypton collected by a solid is directly proportional to the pressure, to the square root of time, and to an exponential function of the temperature (Fig. III-3).

*In any discussion of the specific activity of the Kryptonates, it is important to remember that 5% ^{85}Kr in krypton gas is the most concentrated supply of ^{85}Kr now available. If a gas supply with a larger ^{85}Kr concentration should be made available, kryptonated sources of greater specific activity could be produced and the sensitivity of methods using these materials would be proportionately increased. Oak Ridge National Laboratory has built, and is now testing, a thermal-diffusion plant for the separation of research quantities of ^{85}Kr to yield about 50% ^{85}Kr in krypton gas.

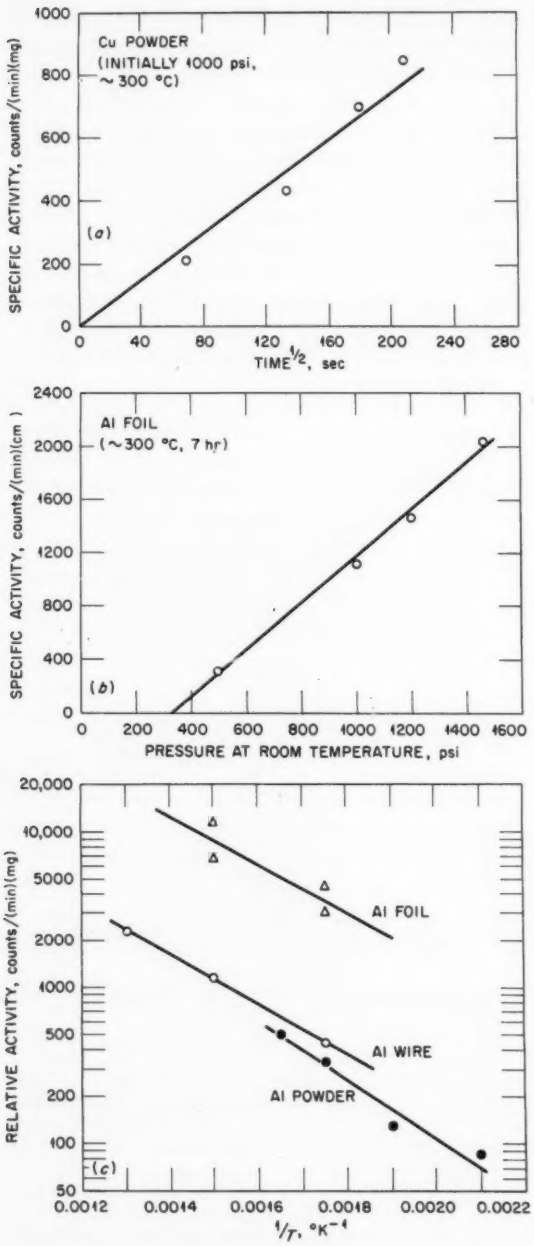


Fig. III-3 Krypton gas collected as a function of (a) time, (b) pressure, and (c) temperature.

Both methods of preparation yield reproducible activity levels. The diffusion technique is generally more versatile. However, Chleck[5] observed that the ion-bombarded materials demonstrate a greater reproducibility in their thermal behavior, the bombardment conditions being easier to control than those of the high-temperature high-pressure diffusion method. Chleck[7] states further that, for the preparation of specific sources such as the kryptonation of only a certain portion of a surface, the ion-bombardment method may prove better adapted.

More than 125 different solids have been successfully kryptonated—elements, inorganic and organic compounds, and alloys—in the form of tubes, lumps, foils, wires, powders, disks, chunks, strings, beads, pellets, fabricated pieces (e.g., pyrolytic-graphite pieces), rods, and insulators. More important than the number or variety of types of solids kryptonated is the fact that every solid tested thus far has collected and retained some krypton.

The most promising solids for preparing kryptonated materials of high specific activity are those which contain regular structural voids on an atomic scale. This availability of void space within the crystal lattice is not a simple function of a single parameter. It depends on the lattice symmetry, lattice point spacing, and the sizes of the atoms or ions occupying the lattice points. The krypton atoms are too large for ordinary interstitial positions in metals and must, in general, occupy lattice points. Some solids—for example, those with the graphite structure—have regular interstitial voids of sufficient dimensions to accommodate krypton atoms. Boron nitride and molecular sieves, which give the highest specific activities (16 and 200 μc/mg, respectively) of the materials produced by Chleck,[7] are materials of this type.

Boron nitride prepared by pyrolysis has the graphite crystal structure of layers of hexagonally arranged atoms superimposed. The lattice dimensions are nearly identical to those of graphite, with an interlayer spacing of 3.36 A and an interatomic distance of approximately 1.4 A within each layer. The size of the resulting superimposed hexagons and their relatively large separation lead to a regular array of void spaces, each large enough to contain an atom of krypton.

Some oxides further complicate the prediction of kryptonating potential because they exist in several crystalline forms, which may vary considerably in free volume.

In a preliminary step of a study to attempt saturation of solids with krypton, Chleck[5] observed that, for a given sample thickness, the specific activity decreased with decreasing grain size. Chleck's data for red iron oxide

[iron(III) oxide, hematite] powder, which is available as a series of known grain-size distributions, were:

Specific surface area, m^2/g	Specific activity, $\mu c/mg$
3.0	2.7
6.0	0.33
9.9	0.10

His tentative explanation is that of the three possible ways in which krypton atoms can occupy positions in a crystal lattice—by substitution, in interstices, or at crystal defects—the predominant occupation in this particular Fe_2O_3 matrix occurs in crystal defects. Since small particles are more nearly perfect crystals, the finer particles would be expected to contain fewer krypton atoms.

Krypton introduced by either method is concentrated near the surface of the host solid. The experimental work of Davies, Friesen, and McIntyre[8] indicated a depth of penetration of approximately 10^3 A by ion bombardment. The depth of penetration by diffusion, 10^3 to 10^5 A, is a square-root function of time and an exponential function of temperature, in addition to being dependent on the host solid. Pressure affects concentration only. The nominal specific activity is the ratio of ^{85}Kr impregnated in the solid to the weight of the solid; the concentration is not uniform throughout the solid.

Chleck[5] achieved saturation of 1-μ platinum dioxide particles with krypton by using 100-hr kryptonation times. Since pressure affects only the concentration, and since maximum temperatures are limited to about 425°C, to prevent decomposition of the platinum dioxide (>450°C), the only process variable is time.

Saturation is confirmed by reacting hydrogen with kryptonated platinum dioxide. The product of the reaction, in addition to platinum and water, is ^{85}Kr in an amount that is directly proportional to the hydrogen concentration. If the ^{85}Kr is located only on the surfaces of the platinum dioxide particles and can be released only in the initial reaction of hydrogen with the particle surface, activity release will reach a maximum and then decrease (part *a* of Fig. III-4). If, however, the particles are completely saturated with ^{85}Kr, that is, they are homogeneously kryptonated, the activity release will remain constant until all the PtO_2 particles are reduced to platinum (part *b* of Fig. III-4). The highly successful, routine production of saturated, homogeneously kryptonated PtO_2 by using long kryptonation times indicates that saturation of other materials with ^{85}Kr by the high-temperature high-pressure diffusion process may be possible.

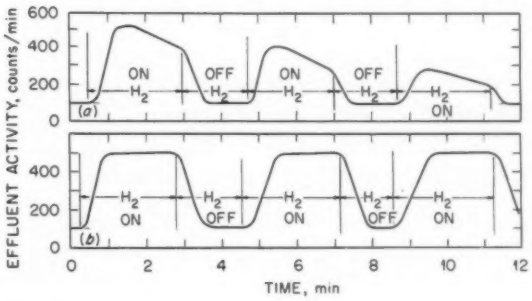


Fig. III-4 Reaction of (a) inhomogeneous and (b) homogeneous kryptonated PtO_2 to 1% H_2 at room temperature.

PROPERTIES

Kryptonates prepared by either method show essentially the same useful and unique properties. They remain stable with time at room temperature, barring surface reactions such as oxidation or hydration of the host solid. According to Leck,[9] who impelled noble-gas ions into a variety of metal targets, the gas is held on the surface and inside the metal as ions or neutral atoms, and desorption within a reasonable period of time requires temperatures of 427 to 527°C. He concluded that the binding energies of the gas within the metal are much higher than those of pure physical adsorption (van der Waals attractive forces).

Even more remarkable is the stability of the Kryptonates at elevated temperatures; that is, a Kryptonate heated to a specific temperature loses a predictable fraction of its initial activity, but there is no further loss of activity with further heating *at* or *below* this temperature. For example, no detectable activity loss occurs[10] during the heating of a kryptonated aluminum-foil sample up to 150°C, but there is an activity loss of 7% as the source is held at 150°C for 1.5 hr (Fig. III-5). During the subsequent heating to 300°C (<0.3 hr), another 15.5% activity loss occurs. Holding at 300°C for 2.2 hr causes

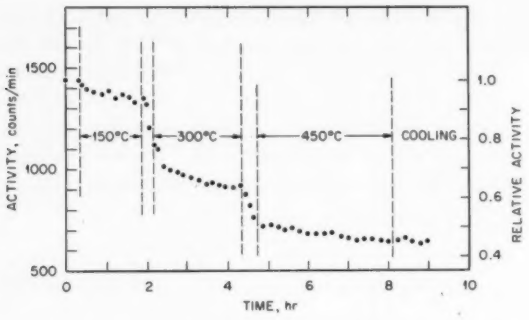


Fig. III-5 Activity losses with time at elevated temperatures for kryptonated aluminum foil prepared by the high-temperature high-pressure diffusion method.

the foil to lose another 14% of its original activity. Heating to 450°C in 0.4 hr and holding at 450°C for 3.3 hr results in additional activity losses of 11 and 7.5%, respectively. In all, this treatment leads to a 55% loss of original activity. When the sample is cooled and left undisturbed for 2 days, there is no discernible activity loss. In fact, there is no loss in activity until the foil is reheated to, and held at, 450°C for 5.2 hr when another 1.5% of the original activity is lost.

Chleck[11] observed that kryptonated pyrolytic graphite heated to 1050°C retained approximately 40% of its initial radioactivity and kryptonated copper foil heated for 0.5 hr at 903°C (180°C below its melting point) retained over 75% of its original activity.

The ^{85}Kr-release temperature threshold varies with the solid and with the method of kryptonation. As an example, Chleck[7] observed that at elevated temperatures the loss behavior of kryptonated copper oxides of approximately equal nominal specific activity varied with the temperature of preparation of the Kryptonate. Some samples prepared at 350°C and 4400 psi lost ^{85}Kr at approximately 350°C, and all showed a loss greater than 50% at approximately 600°C. All samples prepared at 530°C and 3300 psi showed little loss until 700°C when losses greater than 50% occurred. This systematic difference in loss behavior with respect to preparation temperature indicates that this temperature of preparation affects the strength with which the krypton atoms are held.

The Kryptonates are sensitive to chemical or physical disturbances of the surface of the solid, and such disturbances lead to proportional losses of ^{85}Kr. This property is the basis of the use of Kryptonates in chemical analyses. The only requirement is that the host solid react reproducibly with the species being determined. The ^{85}Kr release is proportional to the rate of the chemical reaction taking place, and this reaction rate is a measure of the concentration of the material in question. For example, the amount of water present may be determined by reaction of water with a phosphorus pentoxide kryptonate because the water hydrolyzes P_2O_5.

$$3H_2O + P_2O_5[^{85}Kr] \rightarrow 2H_3PO_4 + {}^{85}Kr$$

To date, no changes following kryptonation have been observed in the chemical properties of the solids. Chleck and Maehl[12] report that preparation of Kryptonates by ion bombardment results in lattice damage at the surface of the solid. They speculate that this may affect some properties of the solid at points where the radioactive krypton concentration is greatest.

The value of the kryptonation technique lies in the special properties of the ^{85}Kr products. These products combine the technical advantages of a high specific activity at the surface with the safety and handling advantages of low total activity. In addition, this "universal" tracer can be incorporated into innumerable solids. It can be used in place of many specific isotopes in applications based on the disturbance of the surface of a solid and can be used to extend such applications to cases where no suitable specific isotope exists.

Applications of the Kryptonates in Chemical Analyses

Kryptonates can be used in radiometric analyses because the ^{85}Kr is released by chemical exchange. The basic requirement for their use in an analysis is that the kryptonated host solid react with the material being determined. The amount of ^{85}Kr released is thus a measure of the concentration of the "unknown" reactant. Chleck and associates[5,7,10,13] developed successful techniques for the determination of aqueous sulfate ion, sulfur dioxide, and oxygen, in addition to the applications and specific analyses discussed below. Chleck's contract called only for demonstration of potential analytical applications but not their full development. Therefore no attempt was made to evaluate precision of the potential methods developed.

AQUEOUS SOLUTIONS

Two methods of application developed by Chleck[7,14] for the analysis of aqueous acid and base solutions are:

1. Reaction of an excess of the aqueous solution with an appropriate Kryptonate (e.g., acid plus zinc kryptonate). The rate of the reaction determines the rate of release of ^{85}Kr, which is a measure of the solute concentration.

2. Reaction of an excess of Kryptonate with a sample of solution. The total ^{85}Kr released, which indirectly is a measure of the mass of the solute, and the volume of solution are used to calculate the solute concentration.

NONAQUEOUS SOLUTIONS

The effectiveness and useful life of many organic solvents, such as fuels and fire-extinguishing fluids, are sensitive to the water impurity content. Since classical titration analyses are proving unsatisfactory[7] in monitoring such liquids, there is considerable interest in developing alternative methods for these determinations.

Chleck[5,7,15] demonstrated the use of Kryptonates to determine traces of water in organic liquids, particularly methanol. He used the apparatus shown in Fig. III-6, the central element of which is the small reaction vessel where an excess of water-sensitive kryptonated calcium carbide is placed. (Experimental runs were carried out with kryptonated barium perchlorate, calcium sulfate, molecular sieves, and silica gel; on the basis of an equal volume of Kryptonate, only barium perchlorate compared favorably with calcium carbide in sensitivity of ^{85}Kr release to water concentration.) The methanol solution is contained in a graduated syringe, which protrudes through a rubber cap, thus permitting the introduction of a sample of the methanol solution while excluding atmospheric moisture. Dry nitrogen is used as a carrier gas for both the ^{85}Kr and the acetylene released during the reaction.

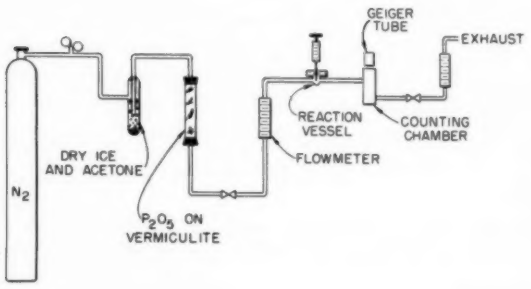


Fig. III-6 Apparatus used in the determination of trace water in methanol.

$$2H_2O + CaC_2[^{85}Kr] \rightarrow Ca(OH)_2 + C_2H_2 + {}^{85}Kr$$

The activity of the total ^{85}Kr evolved is counted as a measure of the quantity of solute that reacted with the CaC_2. From the known volume of the methanol sample, the concentration of water can be calculated. For water concentrations ranging from 0.25 to 2.0% in methanol, a direct proportionality between evolved ^{85}Kr and mass of water was observed.

TITRATIONS WITH KRYPTONATES AS END-POINT INDICATORS

Chleck[7,16] has shown that a kryptonated solid that *does not* react with the solution being titrated but *does* react with the titrant provides a new type of end-point indicator for use where present end-point indicators are not satisfactory. The onset of release of ^{85}Kr from the Kryptonate marks the appearance of excess titrant and, hence, the passing of the equivalence point.

A titration may be carried out in a reaction vessel that contains a magnetic stirrer, the solution to be titrated, and the Kryptonate in the form of a piece of foil. The titration is performed either in steps or at a constant rate of addition of titrant. A gas-line connection to the top of the buret serves to maintain a constant pressure over the titrant. Nitrogen is passed through the reaction vessel to carry the evolved ^{85}Kr to a counter.

The principle and the apparatus were first tested by the performance of a series of titrations of 10-ml NaOH solutions against HCl solutions of the same molarity. Magnesium and zinc kryptonates were used as the end-point indicators, and the titrant was added at a constant rate. Typical recorder traces of effluent radioactivity vs. titrant volume are presented in Fig. III-7.

The sharpness of end points encouraged the application of the technique to a titration for which a better end point is needed. As an example, the value of the technique was demonstrated by the titration of aqueous fluoride ion

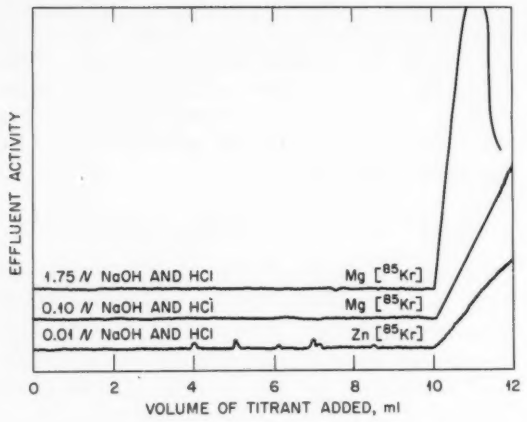


Fig. III-7 Recorder traces of the titration of 10 ml NaOH by HCl with kryptonate end-point indicators.

(as sodium fluoride) by thorium (as thorium nitrate) with zinc kryptonate foil as the end-point indicator.

Chleck suggests that, if the technique of titrating with Kryptonates as end-point indicators is to be used as an accurate analytical method, the time lag during the passage of the ^{85}Kr atoms from the surface of the foil to the counter must be taken into account. Therefore, for this titration, the titrant was added in increments, and each addition was followed by a 4-min counting period. The activity in counts per 4-min interval plotted against the cumulative volume of titrant added gave a titration curve from which the end point could be graphically interpolated. The end point represents the onset of ^{85}Kr release.

Because the titration of fluoride with $Th(NO_3)_4$ is nonstoichiometric, the amount of fluoride must be determined from a calibration curve (Fig. III-8). The accuracy of the method was shown when an "unknown" fluoride solution, made up by adding 25 ml of distilled water to 10 ml of 0.010*N* NaF solution to give a final concentration of 0.0029*N*, was titrated without the operator's knowing the concentration. By graphical interpolation the Kryptonate end point was determined to be 3.125 ml of 0.010*N* $Th(NO_3)_4$ solution, which indicates a concentration of 0.0029*N*.

DETERMINATION OF HAZARDOUS VAPORS

The use of powerful oxidizing and reducing fuels, such as fluorine, chlorine trifluoride, and oxygen difluoride, is becoming commonplace. These highly reactive and beneficial materials are very explosive and toxic, and improper handling of them or faulty equipment can quickly lead to hazardous levels of atmospheric contamination, resulting in loss of life, equipment, and time. An instrument is needed to detect and warn of these gases when their concentrations are still below explosive or toxic levels so that remedial action can be taken immediately.

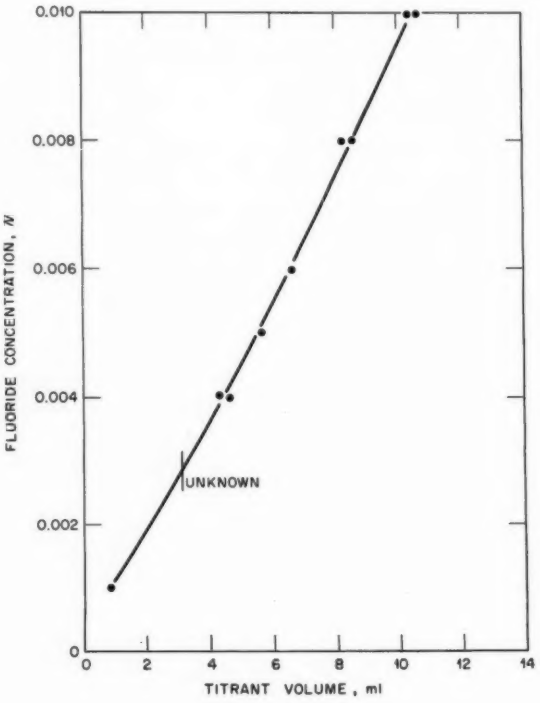


Fig. III-8 Calibration curve of titration of 10 ml NaF by $Th(NO_3)_4$ with Zn[^{85}Kr] as end-point indicator.

In a successful investigation of the determination of traces of hydrogen, Chleck[5,7,11] used a quartz oven as a reaction vessel (Fig. III-9). The oven has a shelf for mounting a kryptonated metallic oxide source and an aluminum window for counting the activity with an external Geiger tube. The temperature of the vessel is controlled by a Nichrome heating coil that surrounds the vessel.

The hydrogen concentration was varied by diluting a 1% H_2 in N_2 mixture with either pure nitrogen or air. Of several kryptonated oxides subjected to various concentrations of flowing

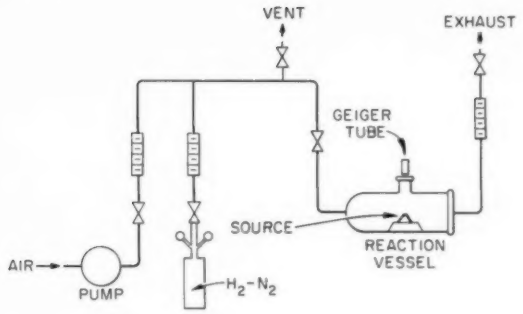


Fig. III-9 Hydrogen detection system.

hydrogen, platinum dioxide was found to give the most sensitive response:

$$2H_2 + PtO_2[^{85}Kr] \rightarrow 2H_2O + Pt + {}^{85}Kr$$

As reduction occurred, ^{85}Kr was released and the percentage of the krypton activity lost was related to hydrogen concentration.

These gas-solid reactions were investigated at both ambient and elevated temperatures. For the elevated-temperature work, the Kryptonates were preheated to a predetermined temperature in a quartz oven so as to make them thermally stable at or below this temperature. The ^{85}Kr was released only by reaction of the solid with hydrogen. Figure III-10 shows the rates of activity loss for kryptonated platinum dioxide at various hydrogen-gas concentrations.

When air instead of nitrogen was used as the diluent, no release of activity was observed. Instead of reducing the metallic oxides, the hydrogen was itself oxidized by oxygen of the air at the oxide surface:

$$2H_2 + O_2 \xrightarrow{PtO_2[^{85}Kr]} 2H_2O$$

This process does not disrupt the surface of the oxide, and thus no ^{85}Kr is released. The catalytic oxidation of hydrogen may be prevented by the use of a coating. Almost any powder had some protective effect:

$$2H_2 + \text{coated } PtO_2[^{85}Kr] \xrightarrow{O_2} \text{coated Pt} + 2H_2O + {}^{85}Kr$$

Aluminum oxide, the best of these materials, resulted in excellent response and sensitivity in an air atmosphere.

These coatings are believed to act by delaying the arrival of the relatively larger oxygen atoms at the oxide surface. The catalytic oxidation of hydrogen is thus inhibited. A corollary of this hypothesis is that the hydrogen arrives at a slower rate in the coated than in the uncoated platinum dioxide. Therefore the response of a coated Kryptonate to the same concentration of hydrogen in an oxygen-free atmosphere should be less than that of an uncoated one. In order to obtain the sensitivity displayed by the uncoated sample at room temperature, it was necessary to raise the temperature of the coated sample to 350°C.

The response of this detection technique varies with the rate of ^{85}Kr release. The greater the rate of loss, the shorter the time necessary for the loss to be measurable. With an Al_2O_3-$PtO_2[^{85}Kr]$ mixture at the maximum operating temperature of 435°C (platinum dioxide decomposes at 450°C), H_2 concentrations of 1% and 10 ppm can be measured in less than 0.5 sec and less than 10 min, respectively.

A successful technique for the detection of fluorine as well as hydrogen is currently being used in a prototype model of an instrument that is capable of detecting low concentrations of hydrogen, fluorine, and fluorine-containing oxidizers.[5,7] The instrument is portable, reliable, simple to use, and suitable for field and laboratory application. It is designed to give an audible alarm within 3 to 5 sec at concentrations of either 0.5 or 1.0% hydrogen and at 0.025 ppm fluorine, chlorine trifluoride, or oxygen difluoride. Basically the detector consists of a Geiger tube and kryptonated sources, each source

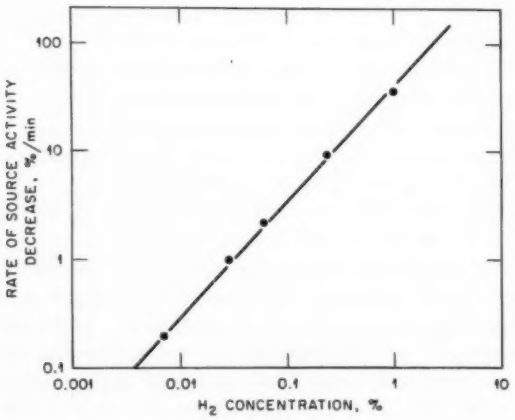


Fig. III-10 Activity loss rates for kryptonated PtO_2 at room temperature and various concentrations of H_2 in N_2.

demonstrating specificity to a particular noxious gas. And the sources will remain stable with time in the absence of reactive gases. Because of the advantages of the detectors, they conceivably may become standard equipment, further extending the use of the Kryptonates and ^{85}Kr. (Joan E. Carden)

Radioisotope Instruments in Industry and Geophysics

An important phase of instrumental radioisotope technology was reviewed extensively in a symposium on Radioisotope Instruments in Industry and Geophysics on Oct. 18–22, 1965, in Warsaw, Poland, and at a panel meeting a few days later (October 25–29) in Cracow. More than 60 papers were presented at the symposium,[17] but only about 25 experts spoke at the panel session.[18] The panel members, nearly all of whom were participants in the Warsaw symposium, made a number of suggestions to the International Atomic Energy Agency (IAEA) about ways in which IAEA could advance the application of radioisotopes for the development of natural resources.

Their report to IAEA gave, in capsule form, the state of the art of radioisotopes instrumentation in geophysics and industry. Abstracts of the Warsaw symposium were published, and the proceedings are in press.

Contributions from the United States were made at both the symposium and panel meeting by G. J. Rotariu, who presented significant aspects of the AEC's Division of Isotopes Development programs in instrumentation. In this section an abridged form of the Rotariu[19] paper is given together with a summary of the Warsaw symposium based on the report and the published abstracts.[20]

The AEC Program in Radioisotope Instrumentation*

Devices and techniques developed by AEC contractors have made significant contributions to radioisotope instrumentation in industry and geophysics. A number of these are discussed, including alpha-excited monoenergetic X-ray sources, beta-excited X-ray fluorescence analyzers, a narrow-band X-ray detector, a sediment density and moisture probe, a methane detector, and a high-head-turbine rating system.

A number of AEC programs have made significant contributions to radioisotope instrumentation. Devices constructed include alpha- and beta-excited X-ray sources for a variety of analyses, a narrow-band X-ray gold detector, a sediment density and moisture probe, and a radioisotope methane detector. In addition to these instruments, a high-head-turbine rating system is discussed.

In 1958 the AEC initiated an accelerated program in isotopes and radiation technology applications. This program, implemented by DID, has resulted in significant achievements.[a] Progress in instrumentation was reported in 1963 to nuclear instrumentation manufacturers.[b] Contributions to advances include alpha- and beta-excited X-ray fluorescence analysis and development of devices and techniques.

ALPHA-EXCITED MONOENERGETIC X RAYS

Chadwick[c] in 1912 discovered the emission of X rays from elements bombarded by alpha particles from a radioactive source. Techniques and instruments have been developed for a variety of applications,[d] including analyzing the heavy elements by X-ray fluorescence and controlling the blending of cement raw materials. Portability and the almost complete lack of bremsstrahlung generation by radiation from these sources have been major factors in their recent development. The availability of monoenergetic X-ray sources in the very-low-energy region (0.2 to 1 kev) probably can extend the realm of X-ray composition measurement to elements of atomic number even below that of magnesium, which is the limit of measurement with the conventional X-ray spectrograph. However, very few experimental data exist on the X-ray yields for the various elements.

Although some gamma photons are produced by these sources, they are a small fraction of the number of alphas — about 1 in 10^5 in the decay of ^{210}Po, for example. These gamma photons are monoenergetic, are generally far removed in energy from the desired fluorescence X-ray line, and can be suppressed by suitable design of source–target geometry. Usable X-ray fluxes from these alpha sources can be produced even

*This is an abridged version of a paper presented by Rotariu[19] at the Warsaw symposium. (The lower case superscript letters, *a* to *t*, refer to Rotariu's reference citations, which are given in the reference section under Ref. 19.)

though those generated by alpha sources are lower than those of beta-excited sources.

Work[e] with alpha sources has demonstrated that characteristic and monoenergetic X radiation can be produced very efficiently. At Parametrics, Inc., use of a 0.69-mc ^{210}Po source with a 0.0008-mm aluminum foil yielded 5×10^5 X-ray photons per minute in the 1.5-kev peak region. Large K_α X-ray yields were measured for carbon, aluminum, titanium, vanadium, iron, and copper (Table III-1). These yields were within the range expected from measured emissions.[f] Important applications of this technique are foreseen in composition analysis, density and thickness measurement, and absorption-edge microradiography. Study of the technical feasibility of using the method for monitoring contaminants in aircraft engine oil is planned.

Table III-1 X-RAY PHOTON PRODUCTION BY ALPHA BOMBARDMENT OF SIX ELEMENTS

(A ^{210}Po Source, 0.69 mc, in a Transmission Configuration and Covered with 0.0043-mm Platinum Foil)

Element	Atomic No.	E_K, kev	X-ray yield, photons	
			Calculated per 5-Mev α/steradian	Measured per 2-Mev α/steradian
Carbon	6	0.28	1.8×10^{-2}	–
Aluminum	13	1.49	1.4×10^{-2}	4×10^{-4}
Titanium	22	4.51	1.3×10^{-3}	1×10^{-5}
Vanadium	23	4.95	–	3×10^{-6}
Iron	26	6.40	4.0×10^{-4}	–
Copper	29	8.05	1.8×10^{-4}	9×10^{-6}

The apparatus shown in Fig. III-11 permits measurements in a controlled atmosphere. The X rays are detected on the same side of the sample that the alphas bombard. The source, 250 mc of ^{210}Po deposited on beryllium, is contained in a variable-aperture collimator. Spectra have been obtained for targets of aluminum, titanium, vanadium (as pentoxide), copper, and molybdenum.

BETA-EXCITED X-RAY-FLUORESCENCE ANALYSIS

The theoretical basis for beta-excited X-ray-fluorescence analysis has been discussed by Cameron and Rhodes[g] and Florkowski.[h] The former workers have investigated a variety of beta-excited sources (^{3}H, ^{147}Pm, ^{85}Kr, ^{204}Tl, and ^{90}Sr–^{90}Y), and Florkowski et al.[i] developed a field device containing a ^{3}H–Zr bremsstrahlung source that measures small amounts of iron and calcium for use in control of blending in the cement industry. These sources were discussed at a recent symposium,[j] and the principles of operation and some applications have been reviewed in earlier issues of *Isotopes and Radiation Technology*.[k]

The first work on use of secondary radiation was done by Morgan, Bizzell, Manov, and Hitch in 1951. They were issued a patent[l] on a beta bremsstrahlung application involving a ^{90}Sr–^{90}Y source, with a lead target, for use as a silt density-measuring device. Later this concept of secondary radiation was further developed by Reiffel and others to emphasize the production of characteristic secondary X rays. A patent[m]

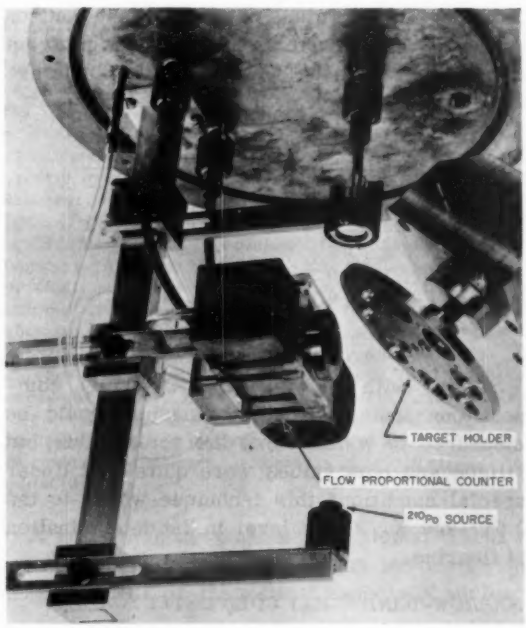


Fig. III-11 Alpha-excited X-ray source and detector assembly.

was issued in 1960 on an apparatus for X-ray-fluorescence analysis.

Martin and Blake,[n] of Texas Nuclear Corporation, are developing and evaluating new types of tritium-excited X-ray sources for analysis of ores and ocean-bottom cores. In one such device the source, a 0.6-cm-diameter disk cut from a 2.5-cm-diameter $^{3}H-Ti$ target material, is positioned on a 0.25-mm-thick tantalum source support, and the assembly is centered on the face of a 0.013-mm-thick beryllium window of a gas-flow proportional counter. For analysis, samples that are thicker than the saturation excitation thickness are successively placed over the window. X rays of energy greater than 1.25 kev are detectable in air, but for lower energies a helium atmosphere is required. A "doughnut" source geometry, instead of the conventional source-on-window setup, is used to increase the counting yield.

A calibration curve for measuring sulfur in coal was obtained by using a series of standards containing from 0.5 to 10 wt.% sulfur in pure powdered graphite. The technique has good possibilities for field use, especially where coal contains a high concentration of elements with atomic numbers close to that of sulfur.

In studies on analysis of ocean-bottom samples, iron determinations by fluorescence agreed well with values obtained by fast-neutron activation analysis, considering the significant interference of the 4.509-kev "backscatter" peak with the iron K_α X rays at 6.4 kev.

Iron, %	
Fast-neutron activation analysis	Fluorescence analysis
1.3 ± 0.3	1.4
1.3 ± 0.3	1.4
3.3 ± 0.7	4.7
6.5 ± 1.3	8.0

Studies with known $MgO-SiO_2-Fe_2O_3$ compositions indicated that magnesium could be measured to within 6% of the actual value, but silicon and iron values were quite low. Under special conditions this technique works to the 0.677-kev K_α X-ray level in the determination of fluorine.

NARROW-BAND X-RAY GOLD DÉTECTOR

A project initiated with Tracerlab 2 years ago has culminated in a successful instrument for detecting gold.[o] A ^{133}Xe source and NaI(Tl) crystal detector are used in the device, which was developed for use by the U. S. Customs Service for the nondestructive testing of articles suspected of containing gold. The 81-kev gamma rays from ^{133}Xe cause gold to emit K_α X rays. Gold content of 1% or higher can be readily detected in a sample. If a plated object is being examined, the gold plating is detected if it is thicker than 2.5×10^{-5} mm. An indication is given on a meter or by a high-frequency whistle. Other sources are being evaluated for gold detection, including ^{109}Cd and ^{155}Eu.

SEDIMENT DENSITY AND MOISTURE PROBE

The density of ocean-bottom cores is usually measured by obtaining samples from the sea floor and taking them to the laboratory for examination. An in situ density-measuring device[p,q] based on the scattering of gamma rays from a radioisotope source has been designed. The unit, built by Lane-Wells Co., can make 60 measurements in an 8-hr day; only 4 or 5 cores can be handled in this time with a standard oceanographic device. In a number of field tests by the U. S. Naval Oceanographic Office in Panama City, Fla., profiles obtained with the radioisotope instrument correlated well with those obtained previously by standard methods.

The radioisotope apparatus is 8 m long, ranges from 7.6 to 15.2 cm in diameter, and weighs 318 kg in air. The main portion is a steel barrel 6.1 m by 9.1 cm that contains a 100-mc ^{137}Cs source, a detector, and electronic equipment. The remaining 1.9 m contain rechargeable batteries and a data-recording system.

In operation the probe is lowered into a penetrable stratum, and the source and detector travel a total of 3.7 m at fixed intervals within the main portion of the barrel. Radiation transmitted directly through the walls of the instrument is scattered by the medium and measured by an assembly of 30 G-M counters. The measurements depend primarily on the electron density of the medium, which, in turn, is related to bulk density. Readings are converted to density from a calibration curve prepared from measurements made by the probe in media of known densities. The instrument is being modified for simultaneous determination of moisture in sediments by a neutron absorption–scattering technique.

A RADIOISOTOPE-ACTIVATED METHANE DETECTOR

Melpar, Inc., has built a methane detector for the U. S. Bureau of Mines. The device, which was discussed briefly earlier,[r] uses an ionization detector.[s] This consists of two parallel tritium-foil electrodes, one of which is connected to a d-c power supply while the other electrode is connected to a d-c amplifier. The output changes with change in gas composition, temperature, or pressure; but in normal coal-mine use, only gas composition will be monitored.

Air is drawn into the apparatus by a small blower through a sintered stainless-steel probe designed to prevent the entrance of coal dust. The air stream is then split; one portion passes through a solenoid valve and sensing detector, the other through a reference detector. The reference and sensing detectors are identical except that they are supplied with voltages of opposite polarity. Since tubing leading to the sensing detector is smaller in volume than that leading to the reference detector, a sudden increase in methane concentration (methane "pocket") will cause the net current output to increase for a short time. A dual-input drift-compensating amplifier is used to achieve a balanced output regardless of imbalance in the two detectors. Concentrations of 1 or 2% methane are sensed.

The methane detector uses solid-state electronic components, is capable of handling any incoming power between 150 and 350 volts, and can be operated by nickel–cadmium batteries for 4 hr after power is shut off.

HIGH-HEAD-TURBINE RATING SYSTEM

The AEC and the Bureau of Reclamation recently began a cooperative program for developing a reliable system for measuring the flow of water through high-head turbines and other hydraulic machines. Optimal techniques for using radioactive tracer materials to measure discharge will be defined, the ultimate goal being to develop an automatic system for calibration of turbines in a dam without shutdown. "High head" refers to water drops of 60 m or greater; "low head" refers to anything less.

Work already done by the U. S. Geological Survey[t] on low-head turbines indicated that ^{198}Au (beta–gamma emitter, 2.7-day half-life) is a useful radiotracer for measuring water volume with a precision of approximately ±1%. A saving of 1% in water flow through the turbines in a major dam, such as the Grand Coulee in the United States, may result in a saving of $1 million to $2 million per year per dam. These savings are a reflection of both the savings in electricity in the area network and in the value of the water distributed downstream.

Research activities initially are confined to laboratory work, a literature search, and preparation of a test manual for field use. Two facilities at the Hydraulic Laboratory of the Bureau of Reclamation at Denver, Colo., are being used. One includes a 20-cm-diameter pipeline 28 m long, and the other has a high-head pump and a cylindrical pressure chamber. Variables of tracer injection, mixing, and sampling and systems for injection of tracers under a pressure of 200 m of water are being studied. Gold-198 as well as other radiotracers of short half-life will be evaluated. Other work includes the development of precision instruments for measuring radioactivity under field conditions.

Summary of the Symposium on Radioisotope Instruments in Industry and Geophysics*

In more than 60 papers presented at the October 1965 Warsaw conference on Radioisotope Instruments in Industry and Geophysics, analysis, gaging, and logging were emphasized. Several contributions from the USSR stressed logging and activation analysis by neutrons and pulsed neutrons in addition to the theoretical aspects of geophysical investigations. A wide variety of devices and techniques in mining, gaging, and analytical applications was discussed by participants from all countries. A few investigators described computer programs and methods for treating complex variables in geophysical studies. Industrial applications covered by other workers included an automated mail-sorting system, measurement and control systems, humidity gages, and thickness and density gages for fibers, metals, and plastics. A number of instruments have been built to determine sediment density, coal ash, and cement constituents. Review papers were presented on the AEC program; measurement and control; instrument design and application; and theory, methods and applications in geophysics.

A number of the papers presented at Warsaw were general in nature, but one set dealt with mathematical or theoretical aspects of nuclear

*This symposium was also briefly reviewed by W. E. Mott, G. J. Rotariu, and C. W. Tittle in *Nucl. News*, 9(2): 20-21 (1966).

geophysics. The Cracow panel reviewed the state of the art in five areas: analysis, gaging, natural-gamma-ray measurements, gamma–gamma logging, and neutron methods. Abstracts of the papers discussed here are listed in the reference section under Ref. 20.

GENERAL

Cameron and Clayton (United Kingdom, abstract 2) reviewed the history, development, and present status of the design and application of radioisotope instruments in industry; discussed the technical advantages of these instruments and the design of sources, detectors, and electronic units; outlined health and safety regulations; explained the physical principles of various gages; summarized the uses of the various instruments in industry; and commented on probable future trends.

Margolinas, Maugest, and Vannier (France, abstract 3) discussed the practical problems encountered in designing, producing, and developing a wide range of radioisotope instruments for measurement and control. Design is no longer a function of some particular task or use in developing radioisotope gages, but of a whole range of practical problems; to solve these problems equipment must be recast in the form of source, detector, and electronic subunits that may be interchanged for various applications. Adapting existing equipment to new uses is sometimes as complicated as designing new equipment. Economic problems involved in producing these instruments also were discussed.

Tittle (United States, abstract 28) and *Alekseev* (USSR, abstract 29) discussed geophysical uses of nuclear devices. In the two decades since the use of gamma-ray survey meters in prospecting started, nuclear applications in geophysics have steadily increased in scope, extent, and importance. Although beta and alpha radiations are sometimes used in geophysics, gamma radiation and neutrons are more widely used (Table III-2).

According to *Alekseev*, the main developments in nuclear geophysics at the present time are:

1. Widespread practical application of methods derived from nuclear physics in geological prospecting, including the use of compact neutron and gamma-ray sources in borehole logging.

2. Intensive prospecting operations and the introduction on an industrial scale of new techniques, based on nuclear physics, for *(a)* quantitative evaluation of the saturation of gas and petroleum reservoirs and for detecting and recording shifts in the contours of gas and petroleum formations during production and *(b)* elementary analysis of rock, especially for quantitatively determining solid mineral resources in samples, excavations, and borings.

3. Intensive development of new and improved apparatus for nuclear geophysics such as neutron and gamma-ray generators, nuclear reactors, multichannel analyzers, and equipment for automatically analyzing and processing the materials obtained.

Table III-2 SOME CURRENT METHODS AND APPLICATIONS OF RADIATION TO GEOPHYSICS

Method	Application
Natural gamma	Surveying for radioelements and delineation of gross geological features
Gamma–gamma	Mass-density determination
Neutron–neutron, neutron–gamma	Determination of hydrogen content (for water); time-dependent measurements with accelerators to locate strong neutron absorbers such as chlorine; detection of a number of elements
Gamma–neutron	Highly specific determination of beryllium

He concluded that future development requires efficient and accurate techniques and instruments, suitable for field work, for the quantitative determination of mineral resources in samples, excavations, and deep borings. Future work will also be concerned with the use of isotopes in the determination of elements in rocks, determinations of absolute age, and the basic problems of groundwater age and dynamics.

THEORETICAL NUCLEAR GEOPHYSICS AND MATHEMATICAL-COMPUTER APPROACHES

Kozhevnikov and Polyachenko (USSR, abstract 58a) reviewed, with an extensive bibliography, the principal results of theoretical investigations in nuclear geophysics in the USSR. Methods of determining, for example, the spatial, energetic, and temporal distribution of neutrons and gamma quanta in a medium of given composition with a given spatial, energetic, and

temporal distribution of the sources are discussed, together with the use of data thus obtained to determine the composition and structure of a substance.

Denisik et al. (USSR, abstract 36) described Monte Carlo calculations for neutron dispersion in rocks.

Heinz and Engelbrecht (South Africa, abstract 37) wrote a computer program for a Monte Carlo calculation of multiple photon scattering according to the Klein–Nishina formula. The Monte Carlo method of random sampling was applied to a geometry closely resembling the configuration of a soil-density backscattering gage. For sources with emission energies greater than 1 Mev, most photons detected were either singly or doubly scattered; thus the functional dependence of the response on the density is mainly determined by the Compton effect. For sources with lower emission energies, where a larger percentage of the detected photons is in the photoelectric effect region, a count–ratio method of presenting results was being studied to reduce the effect of material composition.

Guberman, Izvekova, and Ryabykh (USSR, abstract 51) identify oil-bearing strata in borehole cross sections from industrial geophysical data with the use of a computer with a "learning program" for sample discrimination. Such programs permit objective assessment of the informativeness of methods used in industrial geophysics, including radiometry. Statistical calibration makes possible the acquisition of more information from neutron–gamma logging data than can be obtained when separate reference strata in the borehole cross section are used for calibration.

Guberman, Kozhevnikov, Yakubson (USSR, abstract 35) applied "similitude theory" to the study of radiation transfer processes. The passage of particles through a substance is described by a linear integro-differential equation (transport equation), which can be presented in a dimensionless form. From dimensionless complexes in the equation and in the boundary conditions, a set of independent "similitude criteria" can be derived. These allow (1) extension of the results of theoretical calculations and experimental measurements made for specific conditions to an entire range of similar conditions (Table III-3) and (2) formulation of a principle for modeling radiation transfer problems. These problems include the pattern of change in particle fields as a function of change in the geometry of the medium and its density and, for nonstationary fields, the extent of change with time. Approximate models in nuclear geophysics were formulated for the study of neutron, gamma, and mixed fields in mediums of complex composition with cylindrical interfaces.

Table III-3 CONDITIONS OF APPROXIMATE "SIMILITUDE" FOR NEUTRONS AND GAMMA QUANTA IN VARIOUS ENERGY RANGES

Field	Conditions of equivalency
Neutron	Media of varying composition with regard to moderating properties Fields generated in a medium of given composition by sources with different energy spectra Spectra of epithermal and thermal neutrons with different moderating and absorbing properties Spatial distributions and spectra of thermal neutrons in moderators at different temperatures
Gamma	Media of varying composition with respect to the spatial and energetic distributions of gamma quanta Spatial distribution of soft gamma radiation in a medium of given composition for sources with different spectra

Caldwell, Allen, and Mills (United States, abstract 31) have developed a numerical computer code to solve time-dependent three-group diffusion equations that apply to borehole geometry. The effects of fluid invasion were calculated for estimating the depth of investigation by pulsed neutron logging. Theoretical thermal-neutron lifetimes were obtained for two cases of open-hole fluid invasion—fresh water invading a saltwater-saturated formation and saltwater invading a formation saturated with oil. They discussed the merits of heterogeneous and homogeneous simulation of rock formation in a physical model and evaluated steady-state and pulsed neutron measurements and thermal-neutron lifetimes.

ANALYTICAL INSTRUMENTS

Radioisotope instruments and techniques have been developed for a wide variety of analyses. X-ray-fluorescence analyzers are being used to examine rock surfaces in mines and in mineral prospecting, for laboratory analysis of powdered samples, and for on-stream analysis of powders and slurries. Under favorable conditions the limits of detection range from

0.01 to 0.1%. Backscatter or transmission of electromagnetic radiation and backscatter of beta particles, although nonspecific for individual elements, are routinely used for coal-ash measurement and control of coal-cutting machines. The Mössbauer effect has been used in the analysis of tin ores, and the application to elements other than tin and iron to determine the different phases in which minerals may occur in processing plants is envisaged with low-temperature systems. Other techniques, such as photon activation (see abstracts 59a, 59b), are being refined.

Robin and Darigny (France, abstract 9) reported on the potential use of X-ray fluorescence for the automation of mail sorting. They have built a laboratory prototype of equipment for arranging envelopes so that the addresses are all in the same position. In automated mail sorting this is accomplished conventionally by optical contrast, ultraviolet fluorescence, and other methods (the U. S. Post Office uses "glowing ink" and ultraviolet light to face and cancel envelopes at the rate of about 30,000 an hour). The French device consists of a $^{147}Pm-Al$ bremsstrahlung source that excites the 8.6-kev K_α X ray in zinc that has been added to the stamp-paper pulp. This radiation may be detected by a proportional counter whose pulses are sorted by a single-channel pulse-height analyzer. Each time a letter passes in front of the detector a gate admits pulses to a counting system. If a stamp is present in the area scanned, the number exceeds a predetermined threshold and a triggering pulse signals the letter-routing system. The probability of stamp detection was better than 99%, and the letters could be sorted at the rate of 40,000 an hour.

Rhodes, Packer, and Boyce (United Kingdom, abstract 7) built a portable analyzer for rapid analysis of copper alloys and steels. The device consists of a source, scintillation counter, and transistorized count-rate meter. The counter head used "central source" backscattering geometry and interchangeable filters for energy selection. The instrument is adaptable to X-ray fluorescence, beta-particle backscatter, and X-ray backscatter applications by choice of source, phosphor, and filters. This portable instrument can be used in the metals industry for (1) sorting scrap before re-formation of stock alloys, (2) sorting stocks in the form of ingots, sheets, rods, tubes, and bars, and (3) recognition of components during manufacturing processes, such as extrusion and forging where ordinary markings are obliterated. Results were given for determining molybdenum and lead in steel, and copper and zinc in brass.

Niewodniczański (Poland, abstract 10) used X-ray fluorescence for determining copper deposits in mines. The ^3H-Zr source with differential filters (nickel–cobalt) and a G-M counter determined copper in copper–iron ores with an accuracy of 0.3 to 0.5%. Errors could be appreciably decreased by substitution of a ^{109}Cd source. Results were interpreted nomographically.

Darnley and Leamy (United Kingdom, abstract 11) obtained a series of measurements on several types of tin samples by use of a portable (8 kg) transistorized X-ray fluorescence analyzer: ore pulps, concentrates, heavy mineral sediments, and drill-hole cores.

Starnes and Clark (United Kingdom, abstract 14) designed equipment for the continuous automatic analysis of minerals and ores. Radioisotope X-ray absorption measurements are made continuously on powdered material in the form of a ribbon of constant mass per unit area to determine calcium and iron in process feeds and relative proportions of combustible and mineral matter in solid fuels and boiler residues. A second instrument was developed for continuous analysis of suspensions of fine solids in water by X-ray fluorescence. Up to six parallel flow streams may be analyzed in sequence by a single measuring head under the control of an automatic programmer.

Clayton, Daglish, and Rhodes (United Kingdom, abstract 25) described a system for determining coal ash with particle size of less than about 1 mm. Crushed coal on a small conveyor belt was continuously presented to a radioisotope source–detector assembly consisting of a NaI(Tl) scintillation counter and two ^3H-Zr bremsstrahlung sources. The sources were mounted in a backscatter geometry with respect to the bed of coal whose top surface was automatically smoothed. The intensity of X rays backscattered from the coal indicates the ash content; variations in iron concentration are compensated for by simultaneously counting iron K_α fluorescence X rays. The accuracy of the measurement was ±0.3% ash in the range 0 to 15% ash and ±1% ash for 15 to 50% ash. Measurement time was about 100 sec.

Nagy and Varga (Hungary, abstract 23) have developed a radiological method for determining coal ash. Disturbing effects such as grain size, moisture content, and differences in density were identified and minimized. In a 3-month test at a Hungarian power station, the accuracy, frequency of sampling, continuous measurement, and prompt supply of data produced more information about the total amounts of coal used than did the slower, conventional methods.

Uchida et al. (Japan, abstract 6) developed an X-ray-emission analyzer for controlling mixing of cement raw materials where light elements (magnesium, aluminum, and silicon) exist in a sample matrix of elements of higher atomic number (mainly calcium and a little iron). To analyze the elements of lower atomic number, ^{210}Po was used, and for the elements of higher atomic number, especially iron, a $^{3}H-Zr$ source was used. The sample and the measuring head of the device were kept in vacuum. Two sets of gas-flow proportional counters were used, with or without aluminum filters on each side window, and five sets of single-channel pulse-height analyzers selected pulses of X rays of respective components. Results of measurements were corrected for matrix effect by use of a computer for the control of raw-materials feed. The analysis was more accurate than the usual X-ray fluorescence analysis, and the use of the analyzer was considered better mainly because of economy and rapidity in measurement.

Patterson and Turkevich (United States, abstract 18) determined individual elements from beryllium to calcium on surfaces by alpha-particle scattering. Above calcium, individual elements were not resolved, but groups of neighboring elements were determined together. Sensitivity and resolution were especially high for carbon and oxygen. The method was investigated for application to remote analysis in the space program and for analysis of the composition of thin films. Thicknesses of films in the micron range were measured by analyses of the shapes of the alpha-scattering spectrum.

Kühn and Wiesner (Federal Republic of Germany, abstract 8) developed an apparatus for measuring SO_2, HCl, and Cl_2 concentrations in the exhaust gases of industrial plants. An instrument for continuous gas analysis by X-ray fluorescence was modified for low-molecular-weight materials. The main difficulty, choice of a foil material for the measuring-chamber window that would absorb as little radiation as possible, was solved by construction of a double window constantly flushed internally by hydrogen. For a source containing 2.5 curies of ^{3}H, the detection limits were about 0.1% SO_2, HCl, or Cl_2. An alternative method was developed for continuous determination of SiO_2 and CaO dust. The dust was deposited on a filter paper moving at a constant speed, and the amount of dust was determined by X-ray fluorescence.

Czernecki (Poland, abstract 16) discussed apparatus for measuring the mobility of gases. A six-electrode ionization chamber was irradiated by an active tritium beta source with titanium absorbers. The chamber was polarized by a 1000-volt direct current and by an oscillator generating a frequency varying from a few to a few hundred cycles per second. The current in this chamber at a given frequency depends solely on the number of ions whose mobility can be accurately determined. The mobility is measured by determining the maximum ionization current at a given frequency.

Hallowes and Hodgson (United Kingdom, abstract 19) described a method of measuring the relative humidity of air by the transmission of alpha particles through a very thin film on which an equilibrium amount of moisture is sorbed. A hygroscopic film, specially made from sulfonated cross-linked polystyrene, was mounted on a vane, which was rotated to alternate the film with a nonhygroscopic one. This alternation compensated for changes in pressure and temperature changes of air in the gap and in detector temperature and ensured circulation of air next to the hygroscopic film. The output provided for continuous direct or remote indication, servo control, or recording. The technique is much less dependent on traces of SO_2 than is the standard electrical method. Response is rapid, and the full range of relative humidities at normal atmospheric temperatures is covered. The source, ^{241}Am in a glass bead, gave effectively infinite thickness for alpha-particle self-absorption and negligible contamination hazard. A compact probe was constructed with a small surface-barrier semiconductor detector for measurements in confined places.

Mott and Rhodes (United States, abstract 20) developed instruments and methods using a Pu–Be source for routinely determining the hydrogen content of hydrocarbons by slow-neutron transmission. Hydrogen concentrations

were calculated from a transmission equation using 5-min neutron-transmission measurements and densities determined at the neutron-transmission cell temperature by means of a pycnometer or a low-energy gamma-ray-transmission gage.

Tanemura and Enomoto (Japan, abstract 5) performed X-ray spectrum analysis using a ^{147}Pm beta source. An attempt to use a magnet placed between the specimen and detector to deflect beta particles scattered toward the detector was unsuccessful. In an improved device with high intensity and low background, gold was used to backscatter beta radiation; beryllium foil as thick as 100 mg/cm^2 was placed in front of the window of the proportional counter to absorb scattered beta radiation; and the source, specimen, and counter were arranged to minimize beta radiation to the counter window. Intensities of K_α X-ray emission from chromium, iron, and nickel excited directly by the beta source were from 8 to 12 times as high as those from a beta-excited X-ray source. The determination of chromium and molybdenum in stainless steel gave good results.

Ruegg, Spijkerman, and DeVoe (United States, abstract 17) designed a Mössbauer spectrometer that gives high-precision spectra. The linearity of the instrument used with a voltage-to-frequency converter was within ±0.1% relative standard deviation. A number of applications of this spectrometer were mentioned, including its use in the structural analysis of materials.

Whittaker, Green, and Garnett (United Kingdom, abstract 15) noted that error in the use of gamma absorptiometry for the assay of purified uranium and plutonium in a nuclear fuel reprocessing plant is introduced by interference from light elements and by soft X- and gamma-radiation background from heavy-element solutions. They constructed a detection system subtending a 4π solid angle at the source to reduce the light-element interference. Restricting the path length of the cell to 5 mm and using a carefully designed collimator gave a negligibly small background signal, within certain limitations.

GAGING AND MOISTURE DETERMINATION

Gamma-ray-transmission gages are used extensively in controlling the density and level of liquids and slurries in mineral processing plants, for weighing moving coal or ore wagons, and for measuring the weight of materials on conveyor belts.

Neutron moisture meters are in wide use for measurements in soil, in coke and ores prior to sintering, and in wood chips.

Gamma switches are used for level measurements in open and closed vessels. They are used in mines and surface processing plants as proximity switches on cranes and railway wagons and as safety switches (for example, on coke-oven doors). They are also used for sorting and routing minerals and to sense overloading of conveyor belts.

Miscellaneous devices include ionization smoke detectors, beta gages to measure the accumulations of coal dust, and beta-excited luminous signs in mines.

Caron and Marasse (France, abstract 42) described an interesting use of a neutron surface probe for checking resin injection in salvaging the sandstone temples of Abu Simbel, threatened by the Aswan Dam Project in the United Arab Republic. These temples extend deep into cliffs. They are being sectioned, and single blocks of 15 to 30 tons are being raised 200 ft for reassembly. The blocks are reinforced by injection of a resin capable of cold polymerization so that they will not crack and damage the frescoes inside. The resin is injected on the face opposite the inside wall. Any flow of the resin to the wall might endanger the surface of the frescoes. The surface neutron probe (normally used for humidity determination) is an ideal instrument for locating the resin front at a suitable distance from the wall surface. The sandstone is perfectly dry, but the injected polyester resin contains a high proportion of hydrogen atoms. In preliminary experiments blocks of polyester sand, in different shapes, that had been immersed in silica sand were used to simulate the reinforced rock. The process by which the resin advances, both for a continuous front and for movement along strata of different thicknesses, was reproduced. In the first case, scanning of the surface by a probe gave rise to a constant signal that was perceptible even when the resin was 30 cm from the surface and became stronger as the front approached. In a heterogeneous medium the reading would depend on the position of the probe. Analysis of the curves obtained from these geometric models indicated the feasibility of rapid interpretation of the measure-

ments made during in situ injections into the rock.

Marcesse, Couchet, and Jossoud (France, abstract 41) used the neutron method to measure moisture in grain, chiefly maize, and thus to obtain more information on the conditioning of maize by drying. A moisture meter coupled with an integrator detected the fast neutrons thermalized by the hydrogen atoms in both the water and the organic material, principally starch. This method was particularly suitable for studying the development of the desorption front in a column of grain dried by ventilation. Measurement was rapid, reproducible, nondestructive, and continuous.

Kohn (France, abstract 40) described tests with a neutron probe for controlling the moisture of products to be used for agglomeration in a foundry. Statistical analysis showed a linear relation between the counting results and the moisture content of the mixture. Under the trial conditions (50-mc radium–beryllium source, measurements for 5 min), moisture variations of 0.5% were detected.

Borowczik and Krulikowski (Poland, abstract 44) described equipment for determining resistivity, density, and humidity of soil at depths of down to 10 m without carrying out test drills. Resistivity was measured by a three-electrode d-c system, density by attenuation of gamma radiation from a ^{137}Cs source, and moisture by a neutron probe (plutonium–beryllium). Two or three probes could be driven 10 m into the ground by a pneumatic hammer during an 8-hr period.

Majerczyk and Zuber (Poland, abstract 39) found how changes in dry bulk density and concentration of elements with high absorption cross section influence the apparent soil moisture in neutron moisture-probe measurements. A wide range of dry bulk densities was calculated and presented graphically. The changes in absorption cross section were caused mainly by the presence of such elements as boron, iron, and rare earths in soil, and chlorine in water.

Dietl et al. (Federal Republic of Germany, abstract 43) discussed the use of gamma and neutron scattering in the study of underground aquifers. They made both density and moisture measurements in laboratory tests and specifically studied the influence of a gravel fill surrounding a borehole and its effects on the measurement of the undisturbed soil in the vicinity of the boring.

Papadopoulos and Ziegler (United States, abstract 26) developed a gage, containing a 5-mc ^{109}Cd source, to measure the sediment content of water over the range 500 to 50,000 ppm, with an average sediment density of 2.65 g/cm^3. The gage could operate on internal power and record data unattended for 7.5 days. A weatherproof shore-based control unit was connected by 50 ft of waterproof cable to a submersible measuring head, which could be mounted on a wall or piling at any desired water depth. The head contained a sealed reference cell and a channel through which ambient water flowed. Determination is made of the ratio of X-ray transmission through the reference cell containing water but no sediment. Ten of these gages are being field-tested. The system was developed over a 3-year period under the sponsorship of DID and with the cooperation of the Interagency Sedimentation Project, a group representing 14 U. S. agencies having overlapping interests in sediment measurement.

Cameron and Florkowski (IAEA, abstract 27) developed a simple X-ray-transmission gage for measuring suspended sediment in rivers. The measuring head consisted of a source and a scintillation counter between which passed the water containing the sediment. The probe was lowered into a river and the count rate registered on a portable scaler. Two rugged, streamlined versions have been constructed, one using 2 mc of ^{109}Cd and the other 100 mc of ^{241}Am.

Tabor and Lakosi (Hungary, abstract 46) developed a high-accuracy fluid-density gage. Sensitive, high-stability gamma detectors and electronic amplifiers were designed, and an argon-filled high-pressure ionization chamber (130 atm) was built. They also worked out general relationships connecting the parameters of the system, the disturbing signals, the measurement accuracy, and other variables. The relative density accuracy reached was better than 5×10^{-4} g/cm^3 in experimental investigations.

Jurkiewicz et al. (Poland, abstract 49) determined the spatial concentration distribution of fluidized solids by use of a ^{60}Co source and a special instrument to perform scanning in a given cross section of a pipeline. The method assumed for a sand–water mixture that the

mean density of a hydromixture could be maintained constant for several minutes and that in this time a quasi-static concentration distribution occurred inside the pipeline. One run took about 2 min, and at the time that the measurement was taken, the ratio of solid to fluid was controlled by a radioisotope density gage.

Ōno and Machida (Japan, abstract 38) identified seven sources of error in the density determination of coal and soil by gamma scattering. They extended the measuring range for low-density determinations by making the source–detector separation and the detector length small. When a G-M counter with an effective length of 4 cm and a ^{137}Cs gamma source of 1 mc were used, densities of less than 1.2 g/cm^3 were measured with an accuracy of ±2% in 3 min counting time under optimum conditions.

Czarnecki, Demus, and Kowalik (Poland, abstract 50) described three methods of obtaining linear scales in radioisotope instruments. All three techniques can be used for measuring level by radioisotopic methods and are particularly suitable for measuring high linear displacements where safety considerations make it necessary to use radiation sources of low activity. In the first method, detectors were connected in parallel along the vertical axis of the object to be measured, and computer calculations yielded tables of the optimum dose-rate distribution from a point source for various cases. In the second method, based on the effect of an increase in the effective surface area of the radiation detector, the effective surface area "seen" by the radiation source at different distances from the detector increased with an increase in distance between source and detector. Graphs were plotted from calculations for specific cases. The third method was based on using the linear section of the function describing the dependence of the integrating-circuit (diode pump) output-voltage readings on the magnitude of the parameters measured.

Duftschmid et al. (Austria, abstract 45) described digital methods in thickness gaging. Two systems were described: a thickness gage for fast-moving discontinuous materials and a control device for tube-wall thickness. In the first device, as in the usual transmission gage, the material moved between a beta source and a plastic scintillator counter. When the material passed the beta beam, the counting rate was decreased and this signal started a measuring program. With a 25-mc $^{106}Ru-^{106}Rh$ source, counting rates about 10^3 to 10^5 counts/sec, and a preset time of 1 sec for the measurement, the standard error in thickness value was less than ±0.6% in a factory test for the range from 600 to 1400 mg/cm^2. In the second device a radioactive source was inserted in the tubing, and three detectors were arranged outside. A comparison device consisting of a separate radiation source and detector was provided. This worked with an absorber equivalent to the nominal wall thickness. The detector pulses were fed into binary counters. When the end of each measuring cycle was determined by a preset count signal from the comparison counter, the logarithmic readout of the probe-counters was proportional to the thickness difference between the measured tubing sections and the nominal value. With G-M counters, a counting rate of 500 counts/sec and a measuring time of 10 sec, a standard error of less than ±1% of the wall thickness was achieved.

Kühn and Wiesner (Federal Republic of Germany, abstract 48) developed a radiometric method using a 10-mc ^{204}Tl bremsstrahlung source with a silver target for the continuous cross-section measurement of hot-rolled wires of 8 to 20 mm diameter. In laboratory tests that simulated the working conditions of a rolling mill, wires were heated to about 800°C and oscillated parallel and perpendicular to the source. Calculations showed that 200 mc of ^{204}Tl would be required in rolling mills to reduce the statistical error to ±1.5%, giving an accuracy of ±0.6%.

Trost (Federal Republic of Germany, abstract 24) used a ^{241}Am source to measure steel thicknesses of about 3 mm with a precision of ±0.01 mm using a time constant of 1 sec. With about 6 mm thickness, a 150-mm measuring slit, and a time constant of 1 sec, the precision was ±0.02 mm. Glass prototypes with thicknesses of about 3 mm were measured with a precision of ±0.003 mm with a time constant of 2 sec.

Miwa, Mizukoshi, and Shimizu (Japan, abstract 12) devised a beta-backscatter thickness gage for continuously measuring the thickness of the zinc coating on galvanized steel. The gage, which contained a 1-curie ^{85}Kr source, measured thicknesses from 50 to 100 g/m^2 with a precision of ±2 g/m^2 and from 150 to 200 g/m^2 with a precision of ±4 g/m^2 (includes statistical error). The time constant was 4 sec.

Berry and Tolmie (Canada, abstract 47) described an instrument for measuring thicknesses of synthetic fiber bundles by backscattering low-energy X or gamma radiation from a short length of fiber and measuring the intensity of the backscattered radiation. The main advantage of the system is the maximum sensitivity (relative change in intensity per unit mass change) achieved without compromising fibers having variable cross-sectional shape. The radiation energy required was not critical in the region 20 to 40 kev. Iodine-125 was considered the most suitable radioisotope, and difficulties arising from its relatively short half-life were overcome by automatic standardization. The annual capital source outlay was estimated as being only a small fraction of the economic savings made by the use of the instrument. With a source activity of 10 mc, the relative accuracy of measurement on fibers of 4 mg/cm (3700 denier) was ±2% with a time constant of 1 sec.

NATURAL-GAMMA-RAY MEASUREMENTS

Natural-gamma logs are widely used for stratigraphic correlations and for radioactive, and in some cases nonradioactive, ore prospecting. In special cases, spectrometry of natural gamma radiation is used to identify clays.

Natural-gamma-ray surface prospecting is used to assay samples of naturally radioactive elements such as potassium and uranium in the form of ores and core samples.

Larionov and Shvartsman (USSR, abstract 56) made large-scale laboratory and field measurements of the radioactivity (Ra, Th, ^{40}K) of limestone, dolomite, and other carbonate rocks. Physicochemical and lithologo–petrographic properties were analyzed for all substances subjected to radiometric measurements. The absolute value of natural radioactivity in sedimentary (including carbonate) rocks was found to be considerably lower than previously assumed.

GAMMA–GAMMA LOGGING

Density determinations by gamma–gamma logging are achieved to ±1 to 2% under favorable borehole conditions. The location of detectors at different distances from the source reduces the influence of mud cakes and caverns, and agreement is good between gamma–gamma density logs and density measurements on cores. Errors due to variations in chemical composition can be reduced by choosing a suitable low-energy cutoff, but this choice requires highly stable electronic equipment. The density log is also used for analyzing oil shale, locating heavy elements and coal, estimating coal ash (in combination with neutron logs), and evaluating cement. The method is also used for locating heavy elements in blasting holes and for guiding drills in coal gasification projects. When grain and fluid densities are known, porosity can be calculated from data obtained by gamma–gamma techniques.

The selective gamma–gamma log has been developed for heavy-element prospecting. Its accuracy depends on the element and varies from 1% for iron ore to 0.03 to 0.1% for lead. The method is used in boreholes, in blasting holes, and on mine samples.

Sano and Kanaya (Japan, abstract 30) developed a method for measuring partial shrinkage in a borehole with the use of ^{60}Co pellets, which were shot into the soil around the borehole at various depths. Repeated measurements of depth showed any vertical displacement of the sources by comparison with reference radioactive sources fixed to the wall of the casing pipe at equal intervals. A horizontally directional scintillation detector equipped with a tungsten-alloy slit was used to locate the source precisely.

Czubek and Guitton (France, abstract 32) gave the optimum technical characteristics of a probe to measure the density of uranium ores in situ by the gamma–gamma method. Chemical analyses of samples from uraniferous deposits have shown that there is a precise correlation between mass density and electron density measured under certain conditions. A calibration curve was drawn based on results obtained from a single experimental model of known constant density. The "similarity principle" was used to deal with these results. The shapes of the energy spectrum and calibration curve were influenced by the nature of the radioactive source, the diameter over which probing was effected, the distance between source and detector, and the shape of the shield between source and detector.

Dodd and Droullard (United States, abstract 33) determined the bulk density of uranium ores and associated rocks from boreholes by use of

a slim-hole nuclear logging system and computer interpretation program. They used a gamma–gamma density probe with two scintillation detectors spaced at unequal distances from a ^{60}Co source, a conventional amplifier, and a discriminator–rate meter combination having digital and analog outputs. A second-order polynomial equation related the difference in count rate between long- and short-spaced detectors to bulk density. RHOLOG, a FORTRAN language program written for the IBM-7090 computer, was used.

Czubek (Poland, abstract 34) applied the gamma–gamma method to formation-density logging and to obtaining the average concentration of heavy elements in rocks. The physical principles for the application, as well as the relationships among source–detector spacing, rock density, chemical composition, and the response of the gamma–gamma probe, were considered. Heavy-element concentration was determined with the use of the soft part of the registered scattered-gamma spectrum. These results were independent of rock density.

OTHER NEUTRON METHODS AND ACTIVATION ANALYSIS

The (n,n) and (n,γ) methods are used in oil-well logging to determine the hydrogen content of rocks. Detection of epithermal neutrons is preferred for measuring porosity. The (n,γ) method can be used for elements that are strong neutron absorbers and produce high-energy capture gamma radiation, e.g., chlorine, iron, and manganese. The neutron-lifetime method is used mainly to determine oil–water, gas–water, or gas–oil contacts. Some workers are analyzing borehole strata with neutron generators. Combined logs have been suggested for some borehole measurement, for example, (n,n-thermal) logging to locate metalliferous zones and neutron activation to determine the specific elements.

Instruments are available for both surface and small-diameter boreholes. Neutron activation analysis equipment has been developed for field use; polonium–beryllium sources are suitable for 10 elements.

New techniques are being developed with neutron generators, and on-line use of neutron techniques appears promising. Radioisotope neutron sources are being used to measure hydrogen and boron contents and to analyze ores for iron and other elements. A mobile neutron generator, known as the "silver-snooper," has been developed for ground-surface analysis and may be suitable for sample analysis in a field laboratory.

Yakubson and Eife (USSR, abstract 52) performed elemental analyses of rocks in boreholes by spectrometry of (1) capture gamma radiation, (2) induced-activity gamma radiation, and (3) inelastic-scattering gamma radiation generated when the rock was irradiated with neutrons of different energy spectrums (polonium–beryllium and polonium–boron). They detected iron, nickel, and chromium in borehole cross sections, and, under certain conditions, assessed the content of the individual elements by the first method. The silicon content of various types of silicon-containing rock and the fluorine content of fluorites were determined by the second method. The prospects of using the third method to detect coal in borehole cross sections and to determine its quality were explored.

Béress (Hungary, abstract 21) developed a new procedure for simultaneous determination of manganese, aluminum, and silicon in rocks. A portable 7-curie polonium–beryllium source was used to irradiate 38-g powdered rock samples with slow and fast neutrons simultaneously for 4.6 min. The concentrations were computed from the activities determined in the intervals of 0.4 to 5.4 and 60 to 65 min after irradiation.

Blyumentsev et al. (USSR, abstract 53) discussed the use of capture gamma spectrometry to determine the composition of iron-bearing rocks and ores. The basic steps of the technique were recording the integral (or differential) component of the (n,γ)-radiation intensity in the range characteristic of the capture radiation of iron, and separating the "iron" and "rock" components of the (n,γ)-spectrum by solving a system of two or three linear equations. They also described several types of borehole gamma spectrometers being produced or prepared in the USSR.

Kozhevnikov (USSR, abstract 58b), in a paper on theoretical investigations in nuclear geophysics, discussed the overall pattern and characteristics of the stationary distribution of neutrons. Relationships were established which make it possible, on the basis of experimentally determined characteristics of the neutron properties of a given medium for a polyenergetic source with a given spectrum, to calculate the

characteristics of the same medium for other polyenergetic sources with different spectra.

Five papers were presented from the USSR on a pulsed neutron generator and its applications in nuclear geophysics.

Bespalov, Mints, and Shkolnikov (USSR, abstract 60a) described a neutron logging tube that has been in industrial production in the USSR for the past few years. The $^{3}H(d,n)^{4}He$ reaction was used to generate neutrons in the tube. The ion source and target were contained in a sealed metal–glass tube 35 mm in diameter, 185 mm long, and weighing 110 g. An average neutron yield was 10^{7} n/sec. An external temperature of up to 100°C did not affect its efficiency.

Alekseev and Bespalov (USSR, abstract 60b) used a pulsed neutron generator to determine the position of water–oil and gas–liquid contacts and to investigate their movements as the deposit was worked. The water–oil contact was detected when the mineralization of the intervening water layers was 30 to 50 g of NaCl per liter or higher. The neutron generator was also used to check flooding of a gas-condensate deposit.

Bespalov and coworkers (USSR, abstract 60c) described the main characteristics of pulsed neutron generators for carrying out pulsed neutron–neutron and pulsed neutron–gamma logging. Results were presented for studies of strata with different saturations and porosities and of water–oil contacts in boreholes.

Bespalov (USSR, abstract 60d) described the production model of a pulsed neutron generator for pulsed neutron–neutron logging in oil and gas boreholes. Some of the main characteristics of the borehole equipment are: neutron yield, 10^{7} n/sec; transmission frequency, 400 cycles/sec; pulse length, 50 to 200 μsec; diameter, 10.2 cm; weight, 80 kg; and length, 300 cm.

Srebrodolsky and coworkers (USSR, abstract 60e) mentioned the wide use of pulsed neutron logging in a number of oil- and gas-bearing regions to follow the movement of boundary waters. They considered this method more efficient than standard radiometric or electrical measurements.

Antonov et al. (USSR, abstract 54) determined neutron-diffusion parameters in petroleum and in silicate sand saturated with water for a pulsed neutron generator. Three parameters were simultaneously determined: the lifetime of thermal neutrons in an infinite medium, the thermal-neutron-diffusion coefficient, and the diffusion cooling coefficient.

Shimelevich and coworkers (USSR, abstract 55) compared results obtained by a method using pulsed neutrons and inelastic-scattering gamma quanta with results from a method that avoids excitation of the oxygen nuclei by choice of neutrons of appropriate energy. Increased differentiation between water- and oil-bearing sand was obtained by use of the latter method.

Martin, Hall, and Morgan (United States, abstract 22) designed and constructed a closed-loop nuclear analysis system for on-line continuous determination of elements. The pilot plant facility included a variable-speed conveyor belt, a 100-cu ft storage tank for solids such as coal, and screw conveyors. Another loop system was planned for continuous analysis of liquids. The nuclear analysis system consisted of an automatically controlled neutron generator of the Cockcroft–Walton design, a fast-neutron monitor, two NaI(Tl) spectrometers, and a four-channel data-analysis system. Neutron flux was kept at a preset value by the use of a feedback system from the neutron monitor, and the generator high voltage was servo-controlled at a preset value. Target lifetime was increased by an order of magnitude by the use of a beam-sweeping technique. This system was used to evaluate carbon and oxygen determinations in coal by the fast-neutron inelastic-scattering technique and aluminum and silicon determinations by fast-neutron activation analysis. Compton subtraction techniques were used in the data analysis, and the data agreed with spectral data obtained at the same time with a multichannel analyzer.

Berzin and coworkers (USSR) presented two papers on gamma activation analysis of rock and ore samples. The first (abstract 59a) discussed the construction of automatic equipment for analysis of samples to determine activation products with half-lives of a minute or less. The second (abstract 59b) outlined techniques, procedures, and results of recording instrumental gamma-radiation spectra from the products of the activation of a number of elements by bremsstrahlung from laboratory betatrons. Gamma activation and neutron activation were compared. Also discussed was the possibility of analyzing samples weighing tens or hundreds of grams by this method.

(D. A. Fuccillo, Jr.)

References

Preparation, Properties, and Uses of Kryptonates in Chemical Analyses

1. Radio-Release Techniques, *Isotopes Radiation Technol.*, 1(1): 53-60 (Fall 1963).
2. *a.* D. J. Chleck, F. J. Brousaides, C. Hommel, W. Sullivan, L. Fishbeing, and C. Ziegler, Yearly Report on the Development of Radiochemical Analyzers for Nonradioactive Gases and Study of Radioactive Clathrates, USAEC Report AECU-4493, Tracerlab, Inc., July 1, 1959.
   b. D. J. Chleck and C. A. Ziegler, Gas Monitoring Techniques, U. S. Patent No. 2,968,722, to Tracerlab, Inc., Jan. 17, 1961 (filed May 6, 1957).
3. E. E. Fowler and P. C. Aebersold, Status of the U. S. Program on Isotopes and Radiation Development, *Isotopes Radiation Technol.*, 1(1): 26 (Fall 1963).
4. A. G. Streng and A. V. Grosse, Acid of Krypton and Its Barium Salt, *Science*, 143: 242-243 (1963).
5. D. Chleck, R. Maehl, and O. Cucchiara, Development of Krypton-85 as a Universal Tracer, Extension of Phase III. Areas of Application, Period Covered: Nov. 1, 1963–Oct. 31, 1964, USAEC Report NYO-2757-5, Parametrics, Inc.
6. P. Goodman and M. R. Ronayne, Jr., Use of Kryptonates in Materials Research, Air Force Avionics Laboratory Report AFML-TR-65-66 (AD-464813), Parametrics, Inc., March 1965.
7. D. Chleck, R. Maehl, and O. Cucchiara, Development of Krypton-85 as a Universal Tracer, Continuation of Phase III. Areas of Application, Period Covered: Nov. 1, 1962–Oct. 31, 1963, USAEC Report NYO-2757-3, Parametrics, Inc., November 1963.
8. *a.* J. A. Davies, J. Friesen, and J. D. McIntyre, A Radiochemical Technique for Studying Range-Energy Relationships for Heavy Ions of Kev Energies in Aluminum, *Can. J. Chem.*, 38: 1526-1534 (1960).
   b. J. A. Davies, J. D. McIntyre, R. L. Cushing, and M. Lounsbury, The Range of Alkali Metal Ions of Kiloelectron Volt Energies in Aluminum, *Can. J. Chem.*, 38: 1535-1546 (1960).
   c. J. A. Davies and G. A. Sims, The Range of Na^{24} Ions of Kiloelectron Volt Energies in Aluminum, *Can. J. Chem.*, 39: 601-610 (1961).
   d. J. A. Davies, J. D. McIntyre, and G. A. Sims, Isotope Effect in Heavy Ion Range Studies, *Can. J. Chem.*, 39: 611-615 (1961).
9. J. H. Leck, The Bombardment of Surfaces by Positive Ions, in *Chemisorption*, Symposium Proceedings, North Staffordshire, Keele, 1956, pp. 162-168, Butterworth & Company, London, 1956.
10. D. Chleck, R. Maehl, O. Cucchiara, R. Patel, and E. H. Carnevale, Development of Krypton-85 as a Universal Tracer, Phase I and II. Preparation and Properties of Kryptonates, USAEC Report NYO-9720, Parametrics, Inc., Mar. 26, 1962.
11. D. Chleck, Radioactive Kryptonates: A New Tool for Analysis, in *Radiochemical Methods of Analysis*, Vol. II, Symposium Proceedings, Salzburg, 1964, pp. 273-283, International Atomic Energy Agency, Vienna, 1965 (STI/PUB/88).
12. D. Chleck and R. Maehl, Radioactive Kryptonates—II. Properties, *Intern. J. Appl. Radiation Isotopes*, 14: 593-598 (1963).
13. D. Chleck and O. Cucchiara, Radioactive Kryptonates—III. Applications. The Measurement of Oxygen in the Martian Atmosphere, *Intern. J. Appl. Radiation Isotopes*, 14: 599-610 (1963).
14. D. Chleck, R. Maehl, and O. Cucchiara, Development of Krypton-85 as a Universal Tracer, Period Covered: Apr. 1–Oct. 31, 1962, USAEC Report TID-19366, Parametrics, Inc., Nov. 1, 1962.
15. D. Chleck, R. Maehl, and O. Cucchiara, New Technic for Solution Analysis Employing a "Kryptonate"—Acidity of Aqueous Solutions and Water in Methanol, *Chem. Anal.*, 54(3): 84-85 (1965).
16. R. Maehl, O. Cucchiara, and D. Chleck, Radiometric End Point Detection in Titrations Using a "Kryptonate"—Titration of Fluoride, *Chem. Anal.*, 54(3): 83-84 (1965).

Radioisotope Instruments in Industry and Geophysics

17. *Radioisotope Instruments in Industry and Geophysics*, Symposium Proceedings, Warsaw, 1965, International Atomic Energy Agency, Vienna, in press.
18. *Summary Report and Recommendations of the Panel on Uses of Radioisotopes in the Development of Natural Resources*, Cracow, Poland, Oct. 25–29, 1965. Submitted to IAEA.
19. G. J. Rotariu, Advances in Radioisotope Instrumentation Development: Program of the United States Atomic Energy Commission, in *Radioisotope Instruments in Industry and Geophysics*, Symposium Proceedings, Warsaw, 1965, International Atomic Energy Agency, in press.
    a. P. C. Aebersold, Advances in Radioisotope Production and Utilization in Science and Industry, presented at the *Third United Nations International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1964; E. E. Fowler, Radioisotope and Radiation Utilization by United States Industry: Growth and Trends, *6th Japan Conf. Radioisotopes*, Tokyo, Nov. 16–19, 1964, Abstracts of Papers, p. 3.
    b. G. J. Rotariu and P. C. Aebersold, Instrumentation Development and Trends in the Program of the Division of Isotopes Development, presented at the Nuclear Instruments Manufacturers Meeting, Aug. 13, 1963, Washington, D. C.
    c. J. Chadwick, The γ Rays Excited by the β Rays of Radium, *Phil. Mag.*, 24: 594-600 (1912).
    d. W. Bothe and H. Fränz, Untersuchungen Über die Durch α Strahlen Erregte Röntgenstrahlung, *Z. Physik*, 52: 466-484 (1929); A. Robert and P. Martinelli, Méthode Radioactive d'Analyse par Fluorescence X des Eléments Légers, in *Radiochemical Methods of Analysis*, Vol. II, Symposium Proceedings, Salzburg, 1964, pp. 401-418, International Atomic Energy Agency, Vienna, 1965 (STI/PUB/88). H. Imamura, K. Uchida, and H. Tominaga, Fluorescent X-Ray Analysis with Radioactive Sources for Blending Control of Cement Raw Materials, *6th Japan Conf. Radioisotopes*, To-

kyo, Nov. 16–19, 1964, Abstracts of Papers, pp. 300-301.

e. H. Friedman, Monochromatic X-Ray Source, U. S. Patent No. 2,998,524, Aug. 29, 1961.

f. W. T. Ogier, G. J. Lucas, J. S. Murray, and T. E. Holzer, Soft X-Ray Production by 1.5 Mev Protons, *Phys. Rev.*, 134: A1070-A1072 (1964).

g. J. F. Cameron and J. R. Rhodes, Beta-Excited Sources of Electromagnetic Radiation, in *Radioisotopes in the Physical Sciences and Industry*, Symposium Proceedings, Copenhagen, 1960, Vol. II, pp. 23-39, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/20); J. F. Cameron and J. R. Rhodes, X-Ray Spectrometry with Radioactive Sources, *Nucleonics*, 19(6): 53-57 (1961).

h. T. Florkowski, Use of Radioactive X-Ray Sources in Industrial Absorption and Fluorescent Analysis, *Kernenergie*, 7(3): 172-176 (1964).

i. T. Florkowski, B. Dziunikowski, A. Kosiara, and M. Wasilewska, Analysis of Iron, Zinc, and Copper Ores in the Field and Laboratory by Fluorescence Excited by the $^{3}H/Zr$ Bremsstrahlung, in *Radiochemical Methods of Analysis*, Symposium Proceedings, Salzburg, 1964, Vol. II, pp. 419-429, International Atomic Energy Agency, Vienna, 1965 (STI/PUB/88).

j. P. S. Baker and Martha Gerrard (Eds.), Proceedings of the Symposium on Low Energy X- and Gamma Sources and Applications held at Illinois Institute of Technology Research Institute, Chicago, Ill., Oct. 20–21, 1964, USAEC Report ORNL-IIC-5, Oak Ridge National Laboratory, November 1965.

k. Isotope Technology Development, *Isotopes Radiation Technol.*, 3(2): 88-114; Source Development, *Isotopes Radiation Technol.*, 2(1): 55-71 (Fall 1964).

l. G. W. Morgan, O. M. Bizzell, G. G. Manov, and J. W. Hitch, Radiation Analysis, U. S. Patent No. 2,722,609, Nov. 1, 1955.

m. L. Reiffel, Apparatus for X-Ray Fluorescence Analysis, U. S. Patent No. 2,928,944, Mar. 15, 1960.

n. T. C. Martin and K. R. Blake, A Study of Fluorescent Excitation Using Isotopic X-Ray Emission, USAEC Report ORO-627, Mar. 31, 1965.

o. R. H. Forsyth, Narrow Band X-Ray Detector, in Isotope Systems Development Program Annual Contractors Meeting, Nov. 9 and 10, 1964, USAEC Report CONF-641101, p. 20, February 1965.

p. B. F. Wilson, A Sediment Density Meter, USAEC Report ORO-622, Lane-Wells Co., April 1964.

q. G. H. Keller, Deep-Sea Nuclear Sediment Density Probe, *Deep-Sea Res.*, 12(3): 373-376 (1965).

r. G. J. Rotariu, Radioisotopes Are Here To Stay, *Coal Mining Process.*, 1(7): 38-42 (1964).

s. D. J. Pompeo and J. W. Otvos, Radiological Gas Analysis, U. S. Patent No. 2,641,710, June 1953.

t. G. B. Magin, Jr., and O. M. Bizzell, Some Applications of Radioisotope Technology to Water Resources Investigations and Utilization, *Isotopes Radiation Technol.*, 2(2): 124-133 (Winter 1964–1965); B. J. Frederick, Measurement of Turbine Discharge with Radioisotopes, USAEC Report TEI-855, U. S. Geological Survey, Oct. 16, 1964.

20. Abstracts of Papers, Symposium on Radioisotope Instruments in Industry and Geophysics, Warsaw, Poland, Oct. 18–22, 1965, IAEA Publication SM-68. The following abstracts (numbers in parentheses) are discussed in the present issue of *Isotopes and Radiation Technology:*

(2) J. F. Cameron and C. G. Clayton, A Review of the Design and Application of Radioisotope Instruments in Industry.

(3) S. Margolinas, J. Maugest, and R. Vannier, Problems in the Production and Development of a Wide Range of Radioisotope Gauges.

(4) G. J. Rotariu, Advances in Radioisotope Instrumentation Development Program of the United States Atomic Energy Commission.

(5) T. Tanemura and S. Enomoto, X-Ray Spectroanalysis Using ^{147}Pm Beta-Ray Source.

(6) K. Uchida, H. Tominaga, H. Imamura, and H. Miwa, Light Elements Simultaneous Analyser by X-Ray Emission Method Using Alpha- and X-Ray Sources for Cement Raw Mix Control.

(7) J. R. Rhodes, T. W. Packer, and I. S. Boyce, Rapid Analysis of Copper Alloys and Steels Using a Radioisotope Portable Analyser.

(8) W. Kühn and L. Wiesner, Continuous Gas Analysis by Means of X-Ray Fluorescence.

(9) G. Robin and E. Darigny, The Use of X-Ray Fluorescence for the Automation of Mail Sorting.

(10) J. Niewodniczański, Analysis of Copper Ores in Mine Conditions by X-Ray Fluorescence Induced by Isotope Sources.

(11) A. G. Darnley and C. C. Leamy, The Analysis of Tin and Copper Ores Using a Portable Radioisotope X-Ray Fluorescence Analyser.

(12) H. Miwa, T. Mizukoshi, and M. Shimizu, Beta-Ray Back-Scattered Type Thickness Gauge for Galvanizing Process.

(13) J. Cavailles and P. Martinelli, Continuous Measurement of Galvanization Coatings by Means of X-Ray Fluorescence.

(14) P. E. Starnes and J. W. G. Clark, The Continuous Automatic Analysis of Dry Powders and Aqueous Suspensions Using Radioisotope Techniques.

(15) A. Whittaker, G. Green, and J. E. Garnett, Advances in the Gamma-Absorptiometric Determination of Uranium and Plutonium in Solution.

(16) A. Czernecki, A Gas Ionization Analysis.

(17) F. C. Ruegg, J. J. Spijkerman, and J. R. DeVoe, A Mössbauer Spectrometer For the Structural Analysis of Materials.

(18) J. H. Patterson and A. L. Turkevich, Analysis of Light Elements in Surfaces by Alpha Particle Scattering.

(19) K. H. Hallowes and A. E. M. Hodgson, An Alpha Particle Hygrometer.

(20) W. E. Mott and D. F. Rhodes, Hydrogen Analysis by Slow Neutron Transmission.

(21) M. Béress, The Application of Neutron Ac-

tivation Analysis for the Investigation of Manganesian Rocks.

(22) T. C. Martin, J. D. Hall, and I. L. Morgan, An On-Line Nuclear Analysis System.

(23) M. Nagy and K. Varga, Determination of Ash Content of Coals by Gamma-Ray Transmission Method.

(24) A. Trost, Determination of the Ash Contents of Coal, Thickness Gauging of Glass, Plastics and Metals with Am^{241} γ-Rays.

(25) C. G. Clayton, J. D. Daglish, and J. R. Rhodes, A Coal Ash Monitor with Low Dependence on Ash Composition.

(26) J. Papadopoulos and C. A. Ziegler, Radioisotope Technique for Monitoring Sediment Concentration in Rivers and Streams.

(27) J. F. Cameron and T. Florkowski, A Simple X-Ray Transmission Gauge for Measuring Suspended Sediment Concentration in Rivers.

(28) C. W. Tittle, Applications of Radioisotopic Instruments in Geophysics.

(29) F. A. Alekseev, Present Position and Future Trends in Nuclear Geophysics.

(30) S. I. Sano and H. Kanaya, Observation of Partial Shrinkage of Strata.

(31) R. L. Caldwell, L. S. Allen, and W. R. Mills, Jr., Theoretical and Experimental Model Results in Neutron Lifetime Logging.

(32) J. A. Czubek and J. Guitton, Application of the Gamma-Gamma Method for Determining the Density of Uranium Ores in situ.

(33) P. H. Dodd and R. F. Droullard, A Logging System and Computer Program to Determine Rock Density of Uranium Deposits.

(34) J. A. Czubek, Physical Possibilities of Gamma-Gamma Logging.

(35) Sh. A. Guberman, D. A. Kozhevnikov, and K. I. Yakubson, Applications of the Similitude Theory to the Study of Radiation Transfer Processes.

(36) S. A. Denisik, V. E. Lebedev, B. E. Lukhminsky, and R. A. Rezvanov, Solving Nuclear Geophysics Problems by the Monte Carlo Method.

(37) W. F. Heinz and C. A. Engelbrecht, Comparison of Monte Carlo Calculations of the Parameters Governing the Response of the Nuclear Soil Density Gauge with Experimentally Obtained Values.

(38) H. Ōno and T. Machida, Errors of Gamma-Scattering Density Meter and Its Design for Low Density Measurement.

(39) J. Majerczyk and A. Zuber, The Influence of Composition and Density of Soils on Readings of Neutron Moisture Meters.

(40) A. Kohn, Moisture Control in a Mixture for Agglomeration, Using a Neutron Probe.

(41) J. Marcesse, P. Couchet, and M. Jossoud, Grain Moisture Measurements with Neutrons: Application to the Problems of Conditioning and Storage.

(42) C. Caron and J. Marasse, The Use of a Surface Hygrometer for Checking Resin Injections in Salvaging the Temples of Abu Simbel.

(43) H. Dietl, R. Kehrer, H. Moser, F. Neumaier, and W. Rauert, Observations on the Utilization of the Scattering of Gamma Rays and Neutrons to Investigate Underground Aquifiers.

(44) M. Borowczik and C. Krulikowski, A Probe for the Complex Study of the Physical Properties of Soils.

(45) K. E. Duftschmid, J. Steidl, R. Patzelt, and W. Attwenger, Digital Methods in Thickness Gauging, A. Thickness Gauge for Fast Moving Discontinuous Materials; D. Donhoffer, K. E. Duftschmid, R. Patzelt, and F. Buschbeck, Digital Methods in Thickness Gauging, B. Control Device for Tube Wall Thickness.

(46) P. Tabor and L. Lakosi, High Accuracy Fluid Density Gauge.

(47) P. F. Berry and R. W. Tolmie, Radioisotope X-Ray Backscatter Gauge for Synthetic Fibre Thickness Measurement.

(48) W. Kühn and L. Wiesner, Radiometric Method for Continuous Cross-Section Measurement of Hot Rolled Wires.

(49) L. Jurkiewicz, K. Korbel, K. Przewlocki, and K. Umiastowski, Determination of the Spatial Concentration Distribution of Fluidized Solids in Pipelines by Radiometric Methods.

(50) E. Czarnecki, S. Demus, and S. Kowalik, Measurement Methods to Impart Linearity of Scale to Radioisotope Instruments.

(51) Sh. A. Guberman, M. L. Izvekova, and O. I. Ryabykh, The Informativeness of Nuclear Geophysical Methods Applied to Geophysical Research Data in Identifying Oil-Bearing Strata Using a Learning Programme.

(52) K. I. Yakubson and K. Eife, Use of Neutron-Induced Gamma-Radiation Spectrometry to Investigate the Elemental Composition of Rocks in Boreholes.

(53) A. M. Blyumentsev, I. I. Feldman, G. A. Nedostup, and A. N. Zheltikov, Neutron Radiative Capture Gamma Spectrometry as a Method of Determining the Composition of Iron-Bearing Rocks and Ores.

(54) A. V. Antonov, B. V. Granatkin, Yu. A. Merkulev, V. V. Miller, and Yu. S. Shimelevich, The Use of a Pulsed Neutron Generator to Determine Neutron Diffusion Parameters of Rocks and Fluids.

(55) Yu. S. Shimelevich, E. M. Kadisov, N. V. Popov, and E. I. Rekhin, Results of the Measurement of the Energy Spectra of Gamma Radiation from the Inelastic Scattering of Neutrons in Rock.

(56) V. V. Larionov and M. D. Shvartsman, Natural Radioactivity of Carbonate Rocks.

(57) E. M. Filippov, V. Ya. Zhavoronkov, and B. S. Vakhtin, Studies of the Development of Equipment and a Method for Determining Certain Elements Using Resonance and Thermal Neutrons.

(58a) D. A. Kozhevnikov and A. L. Polyachenko, Theoretical Investigations in Nuclear Geophysics in the USSR.

(58b) D. A. Kozhevnikov, Over-All Pattern and Characteristics of the Stationary Distribution of Neutrons.

(59a) A. K. Berzin, K. F. Kuznetsov, V. V. Sulin, G. Ch. Vitozhents, V. G. Suslov, and S. I. Shornikov, Basic Principles of the Construction of Automatic Equipment for

Gamma-Activation Analysis, and Some Results of Its Use.

(59b) A. K. Berzin, V. V. Sulin, V. I. Belov, G. Ch. Vitozhents, Yu. T. Marlynov, V. G. Suslov, and S. I. Shornikov, Study of the "Instrumental" Gamma Radiation Spectra From the Radioactive Products of Some Photonuclear Reactions as Applied to the Gamma-Activation Analysis of the Composition of Rock and Ore Samples.

(60a) D. F. Bespalov, A. S. Mints, and A. S. Shkolnikov, A Small Neutron Tube for Use in Borehole Logging Equipment.

(60b) F. A. Alekseev and D. F. Bespalov, Results of Using a Pulsed Neutron Generator to Solve Certain Problems of Industrial Geophysics.

(60c) D. F. Bespalov, V. F. Gorbunov, A. I. Kedrov, Yu. P. Lyubavin, F. A. Kurilenko, N. V. Popov, A. B. Spassky, D. M. Srebradolsky, L. Z. Tslav, A. S. Shkolnikov, Yu. S. Shimelevich, and V. V. Laptev, Some Results of the Use of Pulsed Neutron-Neutron and Neutron-Gamma Logging.

(60d) D. F. Bespalov, A Borehole Neutron Generator for Pulsed Neutron-Neutron Logging.

(60e) D. M. Srebrodolsky, V. P. Odinokov, A. V. Kuznetsov, and F. Ts. Denisik, Use of Pulsed Neutron Logging Methods to Study Oil and Gas Boreholes.

Section

IV

Isotopes and Radiation Technology

Food Irradiation

An article by J. S. Lee et al., Combination Processes in Food Irradiation: Use of Food Additives, *Isotopes and Radiation Technology*, 3(1): 42-48 (Fall 1965), considered three classes of additives — antibiotics, radiation sensitizers, and chemical preservatives. The present article is a brief Belgian survey, in more detail, of only one of the classes, radiation sensitizers.

Radiation Sensitizers in the Preservation or Sterilization of Food, Drugs, and Medical Supplies*

By M. de Proost†

Chemicals reported in the literature that enhance radiation inactivation of bacteria are oxygen, alkali halides halogenophenols, vitamin K_5 and its analogs, N-ethylmaleimide, and iodoacetamide. Their effects on bacteria, spores, and yeasts are compared, and the possible technological importance of radiation sensitizers is discussed.

Radiation is now being used in industry on a commercial scale for sterilization of plastic hypodermic syringes, scalpel blades, and other medical supplies. The successful marketing of irradiated potatoes in Canada and the USSR and the clearance for public consumption of radiation-sterilized bacon and radiation-treated grain by the U. S. Food and Drug Administration are events that no doubt will have a very stimulating effect on the whole field of food irradiation.

These facts, together with a number of other realistic applications of ionizing radiation now in sight, are likely to lead to rapid developments in the field of radiation treatment of food, drugs, and medical supplies (Table IV-1).

Applications such as the sterilization of food involve high radiation doses. The criterion adopted for sterilization of nonacid foods is that the radiation dose should be sufficient to inactivate by a factor of 10^{12} the *Clostridium botulinum* spores initially present. This requires a dose of 4 to 5 Mrads. In most food such doses produce chemical changes that give rise to off-odors and off-flavors. An approach worth special attention is sensitization of the microorganisms to radiation to decrease the doses needed for sterilization.

Table IV-1 POTENTIAL APPLICATIONS OF RADIATION PROCESSING

Application	Cause of spoilage	Dose, Mrads
Inhibition of sprouting of potatoes, onions, etc.	Sprouting	0.01
Disinfestation of grain	Insects	0.02
Elimination of food-poisoning organisms in food and feed	*Salmonella*	0.5–1.0
Pasteurization of meat, fish, and fruit	Vegetative bacteria and molds	0.1–1.0
Sterilization of food, food ingredients, drugs, and medical supplies	Vegetative and spore-forming bacteria	1.0–5.0

Radiation Sensitization of Bacteria by Chemicals

The literature names several substances that enhance radiation inactivation of bacteria and that could eventually be of some technological importance: oxygen, alkali halides, halogeno-

*An edited version of The Possibility of Using Radiosensitizers in the Preservation or Sterilization of Food, Drugs, and Medical Supplies by Irradiation, Report BLG-327, November 1964. Presented at IAEA Panel on Molecular Basis of Radiosensitivity, Vienna, Nov. 16–20, 1964.

†Centre d'Étude de l'Énergie Nucléaire, Brussels, Belgium.

phenols, vitamin K_5 and its analogs, N-ethylmaleimide, and iodoacetamide.

OXYGEN

Oxygen sensitizes virtually all biological and many chemical systems to inactivation or to some alteration by ionizing radiation. This well-known response has been termed[1] the "oxygen effect." Radiation sensitivity is proportional to the oxygen concentration,[1–5] and, for a given oxygen concentration, the radiation sensitivity increases exponentially with radiation dose.[6] With X and gamma radiation, the maximum ratio* for enhancement of sensitivity by oxygen has been reported as 2.4 for the haploid yeast *Saccharomyces cerevisiae*;[1] about 3.0 for the bacteria, *Escherichia coli* B,[2] *Escherichia coli* B/r,[1] and *Pseudomonas aeruginosa*;[3] and 2.0 for the bacterial spores of *Bacillus megaterium*.[4] We have found for *Clostridium sporogenes* spores a maximum oxygen effect of 1.8.

ALKALI HALIDES

Okazawa et al.[7–9] found that the sensitivity of cells to radiation was markedly increased by a pre- or posttreatment with 10% NaCl. Their findings led to the hypothesis that the free halogen radicals formed may attack the radiation-sensitive zones near the cell surface or the cell membrane. These authors also found a considerable synergistic reaction to radiation[10,11] with KCl, KBr, and KI. No temperature effect on the halide action was observed, but the removal of oxygen from halide solutions increased the radiation sensitivity of the cells. These actions were observed only during irradiation. For these studies *Zygosaccharomyces soya*, *S. cerevisiae*, and some strains of *E. coli* were used. Practically no sensitization was reported on *Bacillus subtilis* spores.[7]

HALOGENOPHENOLS

Matsuyama et al.[12] investigated the combination of radiation and halogenophenols to increase the lethality of radiation on *E. coli* and *Z. soya*. Some relations between chemical structure and activity were shown at *p*H 6 and 8:

1. Effectiveness of substituted halogen was I > Br > Cl
2. Effectiveness of the monosubstitution position on the benzene ring of halogenophenols was para > meta > ortho
3. Effectiveness increased with increasing number of halogen atoms

The mixture of phenol and halides as a source of free halogen radicals did not enhance the lethality of radiation. Further, the synergistic actions of halogenophenols were greatly decreased by adding certain organic free-radical scavengers (L-cysteine or peptone) or by freezing during irradiation.[13] The indirect actions of ionizing radiations may be involved in the mechanism of enhancement by halogenophenols.

VITAMIN K_5 AND ITS ANALOGS

El-Tabey Shehata[14] demonstrated the ability of 2-methyl-4-amino-1-naphthol hydrochloride (vitamin K_5) to decrease the survival of four species of microorganisms during irradiation. This effect occurred only in a nitrogen atmosphere for the three bacteria *E. coli*, *Micrococcus radiodurans*, and *Pseudomonas fragi*. The yeast *Torulopsis rosea* required aerobic conditions. Vitamin K_5 is not toxic at the levels used ($10^{-4}M$) and has an affinity for sulfhydryl groups; in fact, the effect of vitamin K_5 on radiation sensitivity can be completely neutralized by a sufficiently high concentration of cysteine.

Silverman, El-Tabey Shehata, and Goldblith[15] chose five chemical compounds similar in structure to vitamin K_5 for comparison with vitamin K_5: 4-amino-1-naphthol hydrochloride, 1-amino-2-naphthol hydrochloride, 5-amino-1-naphthol hydrochloride, the tetrasodium salt of 2-methyl-1,4-naphthohydroquinone diphosphoric ester (Synkavite), and 2-methyl-1,4-naphthoquinone sodium bisulfite.

Two of the compounds, 4-amino-1-naphthol hydrochloride and 1-amino-2-naphthol hydrochloride, showed bactericidal action and also increased the lethal effects of ionizing energy to a greater extent than did vitamin K_5 for the test organisms *E. coli* and *Streptococcus faecalis*. However, the toxicity of neither appeared to be correlated to the capability for increasing the lethal effect of radiation. All the compounds were most effective against *E. coli* only in the absence of oxygen. Although *S. faecalis* was influenced both in the presence and in the absence of oxygen, the effect was greater in the absence of oxygen. In addition, 2-methyl-1,4-naphthoquinone sodium bisulfite

*Editor's Note: Reference 1 defines "maximum ratio" as the ratio of the maximum radiation sensitivity at a high oxygen concentration to the anoxic radiation sensitivity.

and 5-amino-1-naphthol hydrochloride were active against *S. faecalis* irradiated in a nitrogen atmosphere. Howard-Flanders and Alper[1] observed earlier that Synkavite had no sensitizing effect on *E. coli*.

Some other naphthol derivatives were also examined by Matsuyama et al.,[12] who found that the synergistic action of unsubstituted β-naphthol was intensified by substitution of halogen for hydrogen. For instance, 1-bromo-2-naphthol and 6-bromo-2-naphthol were more effective than β-naphthol.

N-ETHYLMALEIMIDE

Bridges[16] reported that *E. coli* was sensitized to gamma rays by N-ethylmaleimide in both nitrogen and oxygen, whereas other bacteria were sensitized only when irradiated in nitrogen.[17] According to Bridges the toxicity of N-ethylmaleimide in the presence of radiation may be due to specific combining reactions with vital sulfhydryl groups,[16] and he suggested that the sensitizer was in competition with oxygen.[18]

The effect of this compound on *Serratia marcescens* is clearly sensitization, but only in nitrogen.[19] When cysteine and N-ethylmaleimide were added to the bacteria before irradiation in nitrogen, the sensitizing effect was replaced by a protective effect of cysteine. Thus there is considerable circumstantial evidence that the mechanisms of action of cysteine and N-ethylmaleimide involve a common pathway.

Bridges[18] also reported that N-ethylmaleimide has no action on *E. coli* B/r or on *Pseudomonas* when added after irradiation, but Dewey[19] found a very small but definite sensitization with *S. marcescens*. At the nontoxic level no sensitizing effect[20] for N-ethylmaleimide on *M. radiodurans* was observed in either the presence or the absence of oxygen.

IODOACETAMIDE

A pronounced sensitization of some bacteria was reported by Dean and Alexander[21,22] using iodoacetamide. For the radiation-sensitive bacteria, *E. coli* B and *Pseudomonas fluorescens*, no increase, or only a slight increase, in sensitivity with iodoacetamide ($10^{-4}M$) was found. On the other hand, the more resistant organisms such as *E. coli* B/r and *M. sodonensis* showed a marked increase, and *M. radiodurans*, the most resistant organism studied, showed a most dramatic increase. Time and temperature of treatment with iodoacetamide prior to irradiation did not influence the sensitization. However, the sensitization was lost when the iodoacetamide was removed immediately before irradiation. Apparently iodoacetamide was required to be in the buffered suspension during the irradiation.

The radiation-sensitizing effect of iodoacetic acid on *M. radiodurans* was examined by Lee, Anderson, and Elliker.[20] This product too was effective only when present in the suspending medium during radiation exposure.

Conclusions

The resistance of microorganisms to radiation can be decreased by certain chemicals, but some of the substances considered can hardly be classified as radiation sensitizers; hence it may be more reasonable to assume that the effect of the radiation on the organism is enhanced by the additive. At present the scientific study of radiation sensitization is of greater importance than the immediate industrial applications.

Oxygen is one of the chemicals that could be used in radiation technology, e.g., in the irradiation of medical supplies. However, its application is limited in radiation preservation technology because of the increased damage to the food or pharmaceutical product by oxygen. The use of alkali halides or vitamin K_5 and some of its analogs in the irradiation of food seems to be practical.[7,23]

Especially for food technology, factors other than the radiation-sensitization effect of the chemicals have to be considered, namely, toxicity of the chemical and wholesomeness of the irradiated product. Furthermore, the addition of foreign substances to food is regulated by law, and in most countries the addition of substances with a bactericidal action is forbidden.

More research is needed to evaluate the benefit of radiation sensitizers in radiation technology, especially on the enhancement of the effect of radiation inactivation of bacterial spores. These are the most resistant forms of bacteria that cause spoilage and infection.

References

1. P. Howard-Flanders and T. Alper, The Sensitivity of Microorganisms to Irradiation Under Controlled Gas Conditions, *Radiation Res.*, 7(5): 518-540 (1957).

2. T. Alper and P. Howard-Flanders, Role of Oxygen in Modifying the Radiosensitivity of *Escherichia coli* B, *Nature*, 178: 978-979 (1956).
3. A. A. Van Soestbergen, The Effect of Ionizing Radiation on *Pseudomonas aeruginosa* at Various Concentrations, *Intern. J. Radiation Biol.*, 5(4): 353 (1962).
4. R. B. Webb and E. L. Powers, Water, Glycerol, and Oxygen as Factors in Radiation Sensitivity of Bacterial Spores, pp. 515-516 in Abstracts of Papers for the 9th Annual Meeting of the Radiation Research Society, Washington, D. C., May 15–17, 1961, *Radiation Res.*, 14(4): 445-519 (1961).
5. P. Howard-Flanders, Physical and Chemical Mechanisms in the Injury of Cells by Ionizing Radiations, *Advan. Biol. Med. Phys.*, 6: 553-603 (1958).
6. A. A. Van Soestbergen, The Oxygen Concentration at Which a Response of Specified Magnitude Is Obtained in Irradiation Experiments with *Pseudomonas aeruginosa*, *Intern. J. Radiation Biol.*, 5(6): 567-577 (1962).
7. Y. Okazawa, M. Namiki, S. Yamashita, and A. Matsuyama, Enhancement of the Overall Lethal Effect of Ionizing Radiations on Microorganisms by Sodium Chloride, *Bull. Agr. Chem. Soc. Japan*, 24(3): 235-242 (1960).
8. Y. Okazawa, M. Namiki, and A. Matsuyama, The Mechanism of Radiation Enhancement of the Lethal Effect of Sodium Chloride on Microorganisms, *Bull. Agr. Chem. Soc. Japan*, 24(5): 435-443 (1960).
9. A. Matsuyama, Y. Okazawa, M. Namiki, and Y. Sumiki, Enhancement of Radiation Lethal Effect on Microorganisms by Sodium Chloride Treatment During Irradiation, *J. Radiation Res. (Japan)*, 1(2): 98-106 (1960).
10. M. Namiki, Y. Okazawa, and A. Matsuyama, Combined Effects of Radiation and Inorganic Reagents During Irradiation on Radiosensitivity of Bacterial Cells, *Agr. Biol. Chem. (Tokyo)*, 25(2): 108-114 (1961).
11. M. Namiki, Y. Okazawa, and A. Matsuyama, Modification of Combined Effect of Radiation and Sodium Chloride on Microorganisms by Chemical Agents During Irradiation, *Agr. Biol. Chem. (Tokyo)*, 25(2): 115-123 (1961).
12. A. Matsuyama, M. Namiki, Y. Okazawa, and I. Kaneko, Synergistic Actions of Halogenophenols on Radiation Inactivation of Microorganisms, *Agr. Biol. Chem. (Tokyo)*, 27(5): 349-357 (1963).
13. M. Namiki, A. Matsuyama, Y. Okazawa, and I. Kaneko, Some Aspects of Synergistic Action of Halogenophenols on Radiation Lethal Effect, *Agr. Biol. Chem. (Tokyo)*, 27(5): 358-364 (1963).
14. A. M. El-Tabey Shehata, Effect of Combined Action of Ionizing Radiation and Chemical Preservatives on Microorganisms, *Radiation Res.*, 15(1): 78-85 (1961).
15. G. J. Silverman, A. M. El-Tabey Shehata, and S. A. Goldblith, The Radiosensitivity of *Escherichia coli* and *Streptococcus faecalis* as Influenced by Vitamin K_5 and Its Analogs, *Radiation Res.*, 16(4): 432-440 (1962).
16. B. A. Bridges, Sensitization of *Escherichia coli* to Gamma Radiation by N-ethylmaleimide, *Nature*, 188: 415 (1960).
17. B. A. Bridges, The Effect of N-ethylmaleimide on the Radiation Sensitivity of Bacteria, *J. Gen. Microbiol.*, 26: 467-472 (1961).
18. B. A. Bridges, The Chemical Sensitization of *Pseudomonas* Species to Ionizing Radiation, *Radiation Res.*, 16(3): 232-242 (1962).
19. D. L. Dewey, The X-Ray Sensitivity of *Serratia marcescens*, *Radiation Res.*, 19(1): 64-87 (1963).
20. J. S. Lee, A. W. Anderson, and P. R. Elliker, Radiation Sensitizing Effects of N-ethylmaleimide and Iodoacetic Acid on Radiation Resistant *Micrococcus*, *Radiation Res.*, 19(4): 593-598 (1963).
21. C. J. Dean and P. Alexander, Radiosensitisation of Bacteria with Iodoacetamide, p. 191 in *Abstracts of Papers Presented at the Second International Congress of Radiation Research*, Harrogate, England, Aug. 5–11, 1962. Silver End Documentary Publications, Ltd., London, June 15, 1962.
22. C. J. Dean and P. Alexander, Sensitization of Radio-Resistant Bacteria to X Rays by Iodoacetamide, *Nature*, 196: 1324-1326 (1962).
23. G. J. Silverman, N. S. Davis, and S. A. Goldblith, Modifications of Radiolethality by Vitamin K_5 and Certain Analogs in Model Systems and in Food, *J. Food Sci.*, 28: 687-691 (1963).

Section

V

Isotopes and Radiation Technology

Process Radiation Development

As the potential of the wood–plastics industry is developed, it becomes apparent that many unanswered questions still exist concerning feasibility, efficiency, and overall economics, as well as fundamental questions related to reactions and kinetics of the process itself. Although the need for answers in the latter category is not a deterrent to the general progress of the program, it is certainly of interest to have as much basic information as possible about the process.

Some problems are peculiar to the process of producing wood–plastic compositions—dye uniformity, controlled surface impregnation, retention of resilience in items such as baseball bats, and optimum polymer "loading" for various applications. There also seem to be no clear-cut answers as to how machine irradiation is to be balanced against isotope irradiation. Other problems relate to the wood–plastic products themselves; for example, consumer-acceptance studies are needed, particularly with regard to furniture. A woman who attended a recent wood–plastics meeting (see p. 280, this issue) in Atlanta, Ga., commented about a coffee table, "It's beautiful, but isn't it a little heavy?"

Technical and economic aspects of radiation-produced wood–plastic combinations (WPC) were discussed in a recent issue of *Isotopes and Radiation Technology*.[1] Among the institutions that have studied these materials is McMaster University, where research for a number of years has been concerned with swelling and copolymerization. The techniques used to produce WPC currently being evaluated by the U. S. Atomic Energy Commission (AEC) and industry do not involve swelling of the wood; however, studies have been done under AEC contract on copolymerization[2] and on radiation-induced reactions in swollen polymers,[3] but not in connection with WPC. The AEC has not sponsored work on chemical or thermocatalytic methods for producing WPC.

From time to time there will be reviews of a more fundamental nature to provide "fill-in" for those reviews related more directly to applications. The following report covers, among other things, a study of the graft-copolymerization process in order to determine to what extent it does, in fact, occur. Also underlying this work is the question as to whether WPC prepared by irradiation are appreciably different from the products resulting from a heat-catalyst treatment; i.e., the relative efficacies of radiation-induced and heat-catalyst-induced homopolymerization in wood need to be evaluated, both technically and economically. The editors are unaware of any published work that comprehensively compares WPC prepared by the two methods, although one such study appears to have been started.[4] Should a thermocatalytic process for WPC be developed, it would rise or fall on its ability to compete with radiation. It is interesting to speculate that radiation, which has often challenged conventional techniques for doing a job, may play the role of protagonist for doing this one.

Irradiated Wood–Polymer Combinations

By S. L. Ross* and J. W. Hodgins†

Two techniques of producing wood–plastic combinations (WPC) by radiation have been developed. One of these involves homopolymerization of a plastic inside

*Present address: Chemical Projects Limited, 60 Overlea Blvd., Toronto, Ontario, Canada.

†Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada.

the cell spaces of wood, and the other, copolymerization of plastic with the cellulose of wood. To achieve copolymerization, swelling of the wood is required. Improved properties have been noted in homopolymerized wood, but the swelling needed to produce copolymerized WPC weakens the wood structure so that any gains in physical properties are offset. Since homopolymerization also can be produced by conventional thermocatalytic techniques, it is suggested that the use of radiation to produce WPC by these methods warrants some further investigation.

Although high-energy radiation can be used as an initiator for chemical reactions, such a technique does not produce unique chemicals, and its practical application must always compete with other means of initiation. Accordingly, to achieve reasonable economy, interest has focused on two types of reactions—the chemical chain reaction and reactions yielding products of high-molecular-weight polymers. In this latter type, gamma radiation has been used commercially to produce graft copolymers and cross-linking and to induce "memory" in polymeric materials. It is therefore logical that much work has been done on the gamma-initiated grafting of a large number of monomers to cellulose, the most prevalent of the natural polymers. This is a particularly appropriate application of gamma radiation because it is a relatively efficient process that triggers reaction throughout thick layers of material at moderate temperatures and leaves no catalytic residue as contaminant. From this work the natural step was the investigation of the gamma-initiated copolymerization with cellulose in its natural state—as a constituent of wood.

When this review was written, a good deal of interest was being shown in the wood–polymer combinations (WPC) formed when wood is impregnated with a monomer and the monomer is polymerized in situ by gamma irradiation. Some workers have concentrated on the propensity of gamma radiation for accomplishing graft copolymerization with the cellulose, while others have been using the gamma flux as a catalyst to cause homopolymerization in the cavities of the wood substrate.

Most development in homopolymerization has been done by the group directed by Professor James A. Kent of the Engineering Experiment Station, West Virginia University. A technical and economic appraisal of the process and of the wood–polymer combinations was made by Arthur D. Little, Inc.[5] for the Atomic Energy Commission, and a contract has been placed with the Lockheed-Georgia Company[6,7] for production of pilot quantities of the material for evaluation by the wood fabricating industry. Recently, briefing sessions have been held throughout the United States to familiarize wood fabricators with the advantage of the new material (e.g., Nov. 3, 1965, in Buffalo, sponsored by the Western New York Nuclear Center).

The Effect of Radiation on Cellulose

Pure cellulose undergoes deterioration on irradiation:

1. Appreciable degradation occurs due to chain scission[8–17] at doses of 1 Mrad.
2. Strength and intrinsic viscosity decrease independently of atmosphere or dose rate.[11,13,14,17]
3. Changes seem to be distributed randomly between amorphous and crystalline regions,[9] although there is no decrease in total crystallinity.[13]
4. Carbonyl groups, carboxyl groups, and chain cleavages occur in the ratio 19 : 0.5 : 1 in the atmospheres air, nitrogen, or oxygen.[13,15]
5. Hydrogen, carbon monoxide, and carbon dioxide are evolved in air.[13,15,16]

Because of the protection afforded to the homocellulose by the aromatic structure of the lignin, wood is more resistant to radiation than is pure cellulose.[18] In general, the presence of lignin drastically reduces the number of chain scissions, and this shows up in a gradual reduction of bending strength with gamma dosage.[19]

As might be expected, free radicals result from exposure of cellulose to high-energy radiation. Electron spin resonance (ESR) spectrometry has been extensively used to establish radical population. Some of the findings are:

1. The number of radicals produced is proportional to dose but independent of dose rate.[20,21]
2. The initial ESR hyperfine spectrum is not altered with change in dose, ambient conditions, or degree of cellulose crystallinity.[20–23]
3. Probably two kinds of radicals are present in irradiated cellulose, one with a high electron density on oxygen, the other a carbon-ended radical.[24]
4. At ambient temperatures the radical concentration diminishes with time in two distinct periods—a rapid decrease in concentration in

the first 60 to 75 min followed by a very gradual decay lasting several days.[21–24] At elevated temperatures the radical lifetime is considerably shorter.[22–25]

5. The decay systems in item 4 above represent the decay in actual radical population and not the decomposition of radical peroxides.[21] Oxygen is an aggressive radical scavenger.[20–26]

6. Addition of water or water vapor to irradiated cellulose results in the very rapid disappearance of up to 50% of the free radicals.[11,20,23,26]

Graft Copolymerization with Cellulose

Use of gamma energy presents an attractive means of initiating graft copolymerization to cellulose, particularly if a monomer is chosen which has a lower G value* for radical formation than does cellulose; this is the reason that styrene has received so much attention. Gamma-initiated copolymerization of many monomers with cellulose has been described in a long series of papers. Since such a volume of literature is available, the results of this work are summarized with particular regard to styrene. In particular, significant contributions have been made by Kobayashi,[27] Demint,[28,29] Huang et al.,[17,30–32] Stannett et al.,[26,33–36] and Sakurada.[37]

Reaction conditions and the properties of the resultant polymers have been intensively studied, and the facts here are:

1. No radiation-induced grafting of monomer to cellulose occurs unless a swelling agent is added.[32,33,38,39] Swelling agents used include water, methanol, dimethyl formamide, formic acid, dimethyl sulfoxide, and dioxane. The graft yield seems to depend on the effectiveness of the swelling agent.[17,32,40]

2. In the absence of swelling agents, only homopolymerization occurs.[42]

3. Grafting is initiated by the cellulose free radicals. The presence of the irradiated cellulose causes a sharp increase in the initial polymerization rate because of the juxtaposition of the monomer and the cellulose within the body of the secondary wall. This intimacy decreases the mobility of the growing polystyrene chain and reduces the probability of chain termination. The grafted polymer therefore has a higher molecular weight than that found in the cell cavity.[17,30,31]

4. The resulting copolymer consists of relatively infrequent, but very long, polymer chains; the utilization of potential grafting sites is quite low.[17,30,35]

5. The relatively infrequent grafts do not compensate for the loss in strength due to the breaking of the hydrogen bonds between cellulose chains (authors' unpublished data). Thus the physical properties are not enhanced as a result of the *graft* reaction. Tables of supporting data are given later in this paper.

*The G value is the number of free radicals formed per 100 ev of absorbed energy.

Wood–Plastic Combinations

Wood is an aggregate cellular material of great complexity; each cell consists of long, hollow, tubular fibers, tapered and sealed at each end. The primary wall of the cell forms an envelope for the secondary wall which, in turn, encloses the lumen (cell cavity). The primary wall is highly lignified, whereas the secondary wall is largely cellulose. In the secondary cellulose wall, regions of approximately parallel chains (the crystalline regions) alternate with amorphous regions. The crystalline regions, and to a much lesser extent the amorphous regions, are held together by a large number of hydrogen bonds, while van der Waal's forces make less contribution to the cohesion. When wood is soaked in a pure nonpolar liquid (e.g., styrene or methyl methacrylate), only the cell cavities are filled by the liquid, which is in contact with only the lumen surface. When a polar liquid is added to the impregnating solution, attenuation of the hydrogen bonding occurs and the cell structure relaxes, swells, and permits penetration of the monomer into the cellulosic secondary wall.

The next logical step from investigation of radiation-initiated grafting on cellulose is the investigation of wood as a substrate. The work done with wood falls neatly into two groups: one in which no swelling agent was used and which therefore involves only homopolymerization, and the other in which a swelling agent was used to cause penetration of the monomer into the secondary cell wall and allow for grafting to the cellulose there.

POLYMERIZATION IN THE ABSENCE OF SWELLING AGENTS

Early experiments of this type were described by Karpov and his coworkers,[41] who

reported the enhancement of physical properties by filling the cellular spaces with gamma-polymerized methyl acrylate, methyl methacrylate (MMA), styrene, and acrylonitrile. Improvements in dimensional stability, static-bending strength, and rate of water sorption were cited.

The commercial work now being piloted in the United States, initiated by Kent and his associates, is described in three USAEC reports[42–44] and in *Isotopes and Radiation Technology*.[45] The wood–polymer product is superior to the original wood sample with respect to many physical and mechanical properties. Carbon tetrachloride, a well-known energy transfer agent, effected a dramatic reduction in the dosage necessary for complete polymerization of styrene, methyl acrylate, MMA, and vinyl acetate (VA) in the lumens of the wood.

The rate of polymerization was greater when the monomer was rigorously purified and air was excluded. The rates at which the WPC absorb water, and therefore the rates at which the dimensions are altered, were much lower than for untreated wood.

All the mechanical properties of the WPC, except abrasion, were measured by American Society for Testing and Materials (ASTM) procedures. Three species of wood—white pine, sugar maple, and yellow birch, impregnated with MMA, VA, or a styrene–acrylonitrile solution (60 : 40)—were carefully tested. A regression analysis was applied to yield the results (Tables V-1 to V-3). This study of the mechanical properties indicated that, when the cellular spaces in wood are filled with homopolymer, an improvement in properties occurs over untreated wood:

1. Strength properties are enhanced more in lower strength wood.
2. Hardness improves by a maximum factor of about 3.
3. Compression parallel to grain is enhanced about 50%.
4. Toughness values can be doubled.
5. Abrasion resistance can be more than trebled.

Tests of static bending and shear parallel to the grain yielded somewhat inconsistent values. In general, the property enhancement showed a positive correlation with the polymer loading ratio.

Table V-1 TOUGHNESS DATA FOR WPC[44]

Species	Polymer	Average polymer loading, g polymer/100 g wood	Average relative toughness	Level of significance
White pine	PMMA	36	1.20	*
		68	1.36	†
		100	1.69	†
		144	1.99	‡
	PVA	31	1.22	*
		50	1.46	‡
		83	1.18	*
		109	0.99	N.S.§
Yellow birch	PMMA	20	1.09	N.S.
		41	0.99	N.S.
		67	1.29	‡
		75	1.56	‡
	PVA	14	0.98	N.S.
		37	1.01	N.S.
		55	1.06	N.S.
		73	1.32	†

*Significant at the 5% level.
†Significant at the 1% level.
‡Significant at the 0.1% level.
§N.S., not significant.

Table V-2 ABRASION RESISTANCE OF WPC OF SUGAR MAPLE[44]

Polymer	Polymer loading, g polymer/100 g wood	Relative abrasion resistance
PVA	0	1.00
	14	2.73
	26	1.99
	27	3.84
	53	2.49
	59	3.06
	62	5.39
PMMA	80	3.31
	80	3.64
	82	7.30

POLYMERIZATION IN THE PRESENCE OF SWELLING AGENTS

Chemical bonding between the monomer and the cellulose in wood is possible only upon addition of a swelling agent that permits infiltration of the monomer into the secondary wall.*

A comprehensive report was published in 1962 by Kenaga, Fennessey, and Stannett[47] on the results of radiation-induced polymerization of styrene : dioxane : water (25 : 75 : 5.75 by volume). The findings were:

1. The efficiency of initiation decreases with increasing dose rate.

*The internal area of contact within the secondary wall is more than 1000 times greater than that of the lumen;[46] hence this grafting on the lumen surface is negligible in comparison.

2. Polymer retention increases with increased dose.

3. The amount of time for wafers (2 in. tangential, $1\frac{3}{8}$ in. radial, and $\frac{1}{4}$ in. longitudinal) to reach ultimate swelling in water increases by a factor of about 35.

4. The amount of styrene required for a given degree of stabilization was high relative to the loading used in other methods.

Table V-3 HARDNESS, COMPRESSION, AND STATIC-BENDING AND SHEAR STRENGTH OF WPC OF SUGAR MAPLE[44]

Test	Property	Average polymer loading, g polymer/ 100 g wood	Average relative value
Hardness	Hardness		
Side		26	1.42
		30	1.76
		47	2.92
		56	2.88
End		26	1.52
		30	1.77
		45	2.35
		55	2.55
Compression parallel to grain	Proportional limit	20	1.32
		31	1.34
		46	1.40
	Maximum crushing strength	20	1.15
		31	1.32
		46	1.48
Static bending	Proportional limit	28	1.21
		49	1.18
		56	1.36
	Modulus of rupture	28	1.13
		49	1.23
		56	1.20
	Modulus of elasticity	28	1.05
		49	1.02
		56	1.09
Shear parallel to grain	Ultimate shear	27	1.47
		29	1.24
		43	1.18
		50	1.51

At McMaster University the gamma-initiated grafting of styrene to wood was studied, with the primary objective of improving the physical properties, notably bending strength. This work was initiated by Hodgins and Ramalingam[48] in 1960, continued by Werezak[21] in 1963, and completed by Ross[49] in 1965.

The exploratory work was described by Ramalingam, Werezak, and Hodgins[19,48] using red pine sapwood as the substrate and styrene as the monomer.

For the bending tests a standard ASTM procedure was used, with samples 16 by $\frac{3}{4}$ by $\frac{3}{4}$ in., based on control samples all equilibrated to 76% relative humidity. The results were as follows:

1. A swelling agent was necessary for grafting to occur.

2. The bending load (not modulus of rupture!) was increased about 50%, based on the equilibrated control samples.

3. The penetration rates of water vapor and liquid were drastically reduced, with corresponding stabilization of dimensions.

4. The physical properties of wood in which the cell cavities were filled with homopolymerized styrene were at least as good as those of wood containing graft copolymer.

5. The bending behavior of WPC was independent of the method of initiation (radiation, heat, or catalysis).

6. Free radicals arose in the wood on irradiation, with some transient species persisting for days.

Werezak[21] used experimental procedures similar to those of Ramalingam. Radiation and thermal treatment were optimized with respect to impregnant, composition, total dose, dose rate, temperature, and impregnation procedure. No energy transfer agent (e.g., carbon tetrachloride) was used. The ESR spectrometry was used to make a careful examination of the radical history.

All of Ramalingam's irradiations were carried out in the full beam from the core of the nuclear reactor.

Thermal neutrons activated the manganese in the wood, making it necessary to delay any further treatment (e.g., heating) for 3 to 4 hr after irradiation. In Werezak's experiments this delay was reduced to 15 to 20 min by screening out the thermal neutrons with cadmium. An analysis of Werezak's results[49] made it clear that in these experiments the most important factors with respect to the grafting process are: (1) the concentration of swelling agent in the impregnant solution and (2) the method of impregnation—degree of evacuation, pressure gradient, duration of impregnation—and type of wood (heartwood or sapwood).

Although water acts more or less as a simple swelling agent in the impregnating solutions, methanol plays a more complex role: in addition to promoting the diffusion of styrene into the secondary wall of the cellulose, methanol undergoes radiolysis, and the resultant free radicals increase the rate of homopolymerization. All the results indicated that, when styrene–methanol–water impregnant is used, a "preferential extraction" occurs which has a profound effect on grafting efficiency. In the initial stage of impregnation, the ternary solu-

tion is taken into the lumen; the polar water and methanol are "extracted" by the cellulose in the secondary wall, and, when it has swelled, styrene diffuses into the cellulose, where grafting occurs. This theory was substantiated by high positive correlations between associating efficiency* and monomer uptake (grams of styrene per cubic centimeter of bone-dry wood) and by negative correlations between associating efficiency and specific gravity. Analysis of dimensional changes brought about by the treatment indicated that most of the unextractable polystyrene was located in the cell walls.

Most free radicals generated during irradiation are not utilized in the grafting process. In an attempt to use the graft sites more efficiently, the irradiations of the impregnated wood were performed at elevated temperatures. Hopefully the higher mobility of the monomer would increase the diffusion rate of monomer to the radical sites to an extent that would outweigh the higher rate of radical destruction at the higher temperature. Irradiations were made of wood impregnated with styrene and with the styrene–methanol–water solution, over a temperature range of 39 to 77.5°C, in a "sweep" apparatus.[50] In the cell cavities the kinetics of polymerization and the molecular weight of the polymer were influenced by temperature, as might be expected. However, the transfer of monomer into the cell walls was found to be independent of temperature during irradiation, i.e., an increase in temperature did not increase the extent of the diffusion of styrene into the cell wall. The predominant factor in the grafting process was the swelling of the cell wall beforehand.

The experimental data were reexamined by a regression analysis, which took into account the variations in specific gravity of the wood samples. This procedure eliminated the uncertainty inherent in the comparison of large specimens with the adjoining controls. Accordingly the mechanical properties (as measured by standard ASTM procedures, i.e., equilibration at 76% relative humidity and 25°C) of treated and untreated samples were expressed as a function of the ovendry† specific gravity of the samples prior to treatment. Regression curves for wood and WPC were compared (Fig. V-1).

Although the bending strength of the treated samples was about 50% higher than that of the untreated wood, the modulus of rupture was not

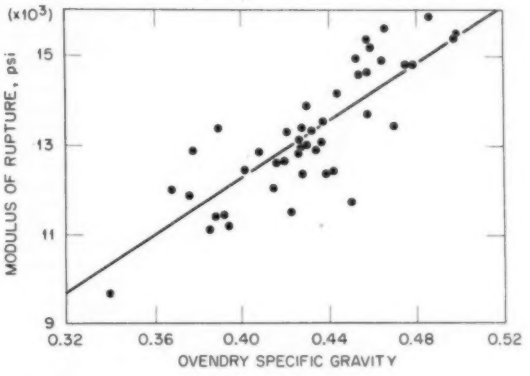


Fig. V-1 Relation between modulus of rupture and specific gravity for humidified red pine sapwood.

improved. This is, of course, due to the dimensional change brought about by the treatment. Other properties relative to static bending treated by regression methods are summarized in Table V-4. Styrene, methanol, and water were used in various volume ratios: 76:22.5:1.5, 65:32:3, and 54:42:4. Dosages ranged from 3 to 5 Mrads.

It is now a well-established fact that wood–polymer copolymers or combinations (i.e., no grafting) absorb substantially less water vapor than unmodified wood when placed in a humid atmosphere. However, the standard ASTM tests used by the McMaster group, and by others, required that controls and test specimens be equilibrated to the atmosphere whose relative humidity is 76%. Accordingly, during testing, the controls have a much higher water content than do the impregnated specimens. Since water has a degrading effect on the strength properties, the comparison is questionable because of the widely different water contents. To establish validity, samples must be compared on the basis of equal moisture content. This comparison was made by oven-drying all samples before testing (Table V-5). On the ovendry basis the modulus of rupture for a sample treated with the 54:42:4 styrene: methanol: water solution (4.0 Mrads) is 23.8 ± 8.1% less than that of the untreated wood. Thus a sample that shows an apparent enhancement of the

*Number of grams of polymer not extracted by hot benzene per gram of total polymer in the treated wood.

†Dried to constant weight at 105°C and 1 atm.

Table V-4 STRENGTH PROPERTIES OF OVENDRIED, HUMIDIFIED, IRRADIATED, AND IMPREGNATED WOOD (BASIS: HUMIDIFIED WOOD)*

Strength property	Altered wood treatment	Change in property, %
Modulus of rupture	Ovendried	38.4 ± 3.9
	Irradiated (3.5 Mrads), humidified	−3.7 ± 2.9
	Irradiated (4.5 Mrads), humidified	−9.9 ± 3.7
	Impregnated (54 and 65% styrene solutions), irradiated, and humidified	Nil
	Impregnated (76% styrene solutions), irradiated, and humidified	Nil
	Impregnated (pure styrene), irradiated (4.5 Mrads), and humidified	56.8
	Impregnated (pure styrene), heated (105°C, 24 hr), and humidified	56.0
Stress at proportional limit	Ovendried	35.9 ± 6.2
	Impregnated (54 and 65% styrene solutions), irradiated, and humidified	25.1 ± 6.2
Modulus of elasticity	Ovendried	Nil
	Impregnated (54 and 65% styrene solutions), irradiated, and humidified	−16.3 ± 4.5
Work to proportional limit	Ovendried	77.8 ± 10.9
	Impregnated (54 and 65% styrene solutions), irradiated, and humidified	78.2 ± 12.2
Work to maximum load	Ovendried	37.3 ± 18.7
	Impregnated (54 and 65% styrene solutions), irradiated, and humidified	−17.9 ± 15.5

*Data presented with 95% confidence limits; except where noted, dose was 4 Mrads.

modulus of rupture under the standard ASTM conditions is found to be inherently weaker than the untreated wood when the comparison is made at identical moisture contents.

Although bending strength is a frequent criterion of the strength of wood, it is really not satisfactory for comparing the structural differences between graft- and homopolystyrene-loaded wood. This is because the bending operation brings into play two primary stresses, tension and compression. An increase in tensile strength and a decrease in the compressive strength can give the misleading impression that little change in the strength properties has occurred. For this reason, tension and compression tests were performed (Table V-6).

Table V-5 STRENGTH PROPERTIES OF OVENDRIED, IMPREGNATED WOOD (BASIS: OVENDRIED WOOD)*

Strength property	Wood treatment†	Change in property, %
Modulus of rupture	A	−23.8 ± 8.1
	B	−6.4 ± 6.2
Stress at proportional limit	A	0
	B	38.3 ± 6.3
Modulus of elasticity	A	−13.9 ± 4.7
	B	0
Work to proportional limit	A	70.4 ± 34.2
	B	63.8 ± 24.9
Work to maximum load	A	−33.2 ± 16.2
	B	−40.0 ± 14.4

*Data presented with 95% confidence limits.

†A, impregnated with styrene: methanol: water (54:42:4 by volume), irradiated (4 Mrads), and ovendried. B, impregnated with pure styrene, irradiated (4 Mrads), and ovendried.

Conclusions

To date no process has been discovered which results in a high frequency of grafting to the cellulose macromolecule in wood. Neither has any evidence appeared that graft copolymerization with the cellulose results in a substantial improvement of the structural properties beyond those which can be obtained by filling the cell cavities with homopolymer. We have found no evidence that the irradiated wood–homopolymer combination is in any way

Table V-6 STRENGTH-PROPERTY DATA OF OVENDRIED, IMPREGNATED WOOD (BASIS: HUMIDIFIED WOOD)

Strength property	Altered wood treatment*	Change, %
Maximum tensile strength	Impregnated (54% styrene solution), irradiated, ovendried	−31 ± 7.3
	Impregnated (pure styrene), irradiated, ovendried	Nil
Maximum crushing strength	Ovendried	57.4 ± 3.4
	Impregnated (54% styrene solution), irradiated, ovendried	17.3 ± 5.3
	Impregnated (pure styrene), irradiated, ovendried	47.1 ± 10.3

*Dose was 4 Mrads.

superior to the combination where the polymerization has been catalytically initiated (unpublished observations).[48,49]

The use of irradiation to initiate polymerization in wood would certainly be justified if a superior copolymerized product had resulted; radiation is particularly applicable in this reaction. However, circumstances dictate that, to achieve copolymerization, swelling agents must be employed, and we have found that the very use of these swelling agents weakens the wood to an extent that outweighs the strength contribution of the graft copolymer. Accordingly there seems to be little point in straining for the copolymer.

On the other hand, the filling of the cell cavities with homopolymer can be accomplished catalytically as well as by gamma initiation, and the two processes yield products, at least on a laboratory scale, of similar strength properties and dimensional stability.[48,49] For this reason the employment of gamma radiation merely as a homopolymerization catalyst is brought into question. Even if the energy cost itself is not high, large-scale irradiation units cannot easily be distributed widely, and the shipping cost of lumber to and from a central irradiation facility will be significant. Thus the lower cost of gamma energy needs to be balanced against simplicity of plant installation and actual processing costs by a catalytic method. In the opinion of the authors, therefore, a more thorough investigation should be made of the thermocatalytic process to produce WPC.

References

1. *Isotopes Radiation Technol.*, 3(2): 115-146 (Winter 1965–1966).
2. Radiation-Induced Polymerization, *Isotopes Radiation Technol.*, 3(1): 49-58, 63-65 (Fall 1965).
3. Zoila Reyes, Radiation-Induced Reactions in Swollen Polymers, Final Report, USAEC Report SRIA-120, Stanford Research Institute, Nov. 30, 1963; M. A. Golub and R. L. Walrath, Radiation-Induced Reactions in Swollen Polymers, Annual Report, USAEC Report TID-18126 (SRIA-103), Stanford Research Institute, Nov. 30, 1962.
4. J. A. Meyer, Treatment of Wood-Polymer Systems Using Catalyst-Heat Techniques, *Forest Prod. J.*, 15(9): 362-364 (1965).

Irradiated Wood–Polymer Combinations

5. F. D. Iannazzi, P. L. Levins, F. G. Perry, Jr., and R. S. Lindstrom, Technical and Economic Considerations for an Irradiated Wood-Plastic Material, USAEC Report TID-21434, Arthur D. Little, Inc., Sept. 1, 1964.
6. Preserving Wood's Market, *Chem. Week*, pp. 117-125 (Aug. 14, 1965).
7. Plastics Wedded with Wood via Atomic Radiation, *Chem. Eng.*, 72(17): 64-66 (1965).
8. C. S. Shoepfle and L. A. Connell, Effect of Cathode Rays on Hydrocarbon Oils and on Paper, *Ind. Eng. Chem.*, 21(6): 529-537 (1929).
9. J. F. Saeman, M. A. Millett, and E. J. Lawton, Effect of High Energy Cathode Rays on Cellulose, *Ind. Eng. Chem.*, 44(12): 2848-2852 (1952).
10. A. Charlesby, The Degradation of Cellulose by Ionizing Radiation, *J. Polymer Sci.*, 15: 263-270 (1955).
11. R. E. Glegg and Z. I. Kertesz, Effect of Gamma Radiation on Cellulose, *J. Polymer Sci.*, 26: 289-297 (1957).
12. R. E. Glegg, The Influence of Oxygen and Water on the After-Effect in Cellulose Degradation by Gamma Rays, *Radiation Res.*, 6: 469-473 (1957).
13. F. A. Blouin and J. C. Arthur, Jr., The Effects of Gamma Radiation. I. Some of the Properties of Purified Cotton Irradiated in Oxygen and Nitrogen Atmospheres, *Textile Res. J.*, 28: 198-204 (1958).
14. J. C. Arthur, Jr., II. Proposed Mechanism of the Effects of High Energy Gamma Radiation on Some of the Molecular Properties of Purified Cotton, *Textile Res. J.*, 28: 204-217 (1958).
15. F. A. Blouin and J. C. Arthur, Jr., Degradation of Cotton in an Oxygen Atmosphere by Gamma Radiation, *J. Chem. Eng. Data*, 5: 470-475 (1960).
16. J. C. Arthur, Jr., F. A. Blouin, and R. J. Demint, The Effects of Gamma Radiation on Cotton Cellulose, *Am. Dyestuff Reptr.*, 49: 383-388 (1960).
17. R. Y.-M. Huang, Radiation-Induced Graft Copolymers of Cellulose, Ph. D. Thesis, University of Toronto, 1963.
18. D. M. Smith and R. Y. Mixer, The Effects of Lignin on the Degradation of Wood by Gamma Irradiation, *Radiation Res.*, 11: 776-780 (1959).
19. K. V. Ramalingam, G. N. Werezak, and J. W. Hodgins, Radiation-Induced Graft Polymerization of Styrene in Wood, in *Proceedings of the Fourth Cellulose Conference, October 18–19, 1962*, R. H. Marchessault (Ed.), Interscience Publishers, Inc., New York, published as a supplement to *J. Polymer Sci., Pt. C: Polymer Symposia*, No. 2, pp. 153-167 (1963).
20. O. R. Bernard, D. Gagnaire, and P. Servoz-Gavin, Mise en Évidence de Radicauz Libres de Nature Differénte Formés dans L'Irradiation aux Rayons Gamma de la Cellulose: Application a la Greffe, *J. Chim. Phys. Chim. Biol.*, 60: 1348-1354 (1963).
21. G. N. Werezak, Radiation-Induced Graft Copolymerization in Wood, M.Eng. Thesis, McMaster University, 1963.
22. S. Kawase, Radicals Produced in Irradiated Cellulose, Annual Report of the Japanese Association for Radiation Research on Polymers, USAEC Report AEC-tr-6316, pp. 100-104, 1964.
23. R. E. Florin and L. Wall, Electron Spin Resonance of Gamma-Irradiated Cellulose, *J. Polymer Sci., Pt. A: General Papers*, No. 1, pp. 1163-1173 (1963).
24. R. E. Florin, Electron Spin Resonance of Gamma-Irradiated Cellulose, in *Abstracts of Papers, 138th National Meeting, American Chemical So-*

ciety, Sept. 11–16, 1960, New York, *Abstr.* 39, p. 16E.

25. H. Ueda, Z. Kuri, and S. Shida, Electron Spin Resonance (ESR) of Radicals Produced in Saccharides by γ-Irradiation, *Nippon Kagaku Zasshi*, 82: 8-11 (1961); *Chem. Abstr.*, 55: 17232h.
26. R. E. Kesting and V. Stannett, The Pre-Irradiation Grafting of Styrene onto Cotton Cellulose Using Gamma Rays, *Makromol. Chem.*, 55: 1-14 (1962).
27. Y. Kobayashi, Gamma-Ray-Induced Graft Copolymerization of Styrene onto Cellulose and Some Chemical Properties of the Grafted Polymer, *J. Polymer Sci.*, 51: 359-372 (1961).
28. R. J. Demint, J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, Radiation-Induced Interaction of Styrene with Cotton, *Textile Res. J.*, 32: 918-922 (1962).
29. J. C. Arthur, Jr., and R. J. Demint, Properties of Cotton Containing Radiation-Polymerized Acrylonitrile, *Textile Res. J.*, 30: 505-509 (1960).
30. R. Y.-M. Huang, Discussion after paper by Y. Kobayashi, *J. Polymer Sci.*, 51: 368-371 (1961).
31. W. H. Rapson, R. Huang, B. Immergut, and E. H. Immergut, Grafting onto Cellulose, in *Abstracts of Papers, 138th National Meeting, American Chemical Society*, Sept. 11–16, 1960, New York, *Abstr.* 28, p. 11E; R. Huang, B. Immergut, and W. H. Rapson, Cellulose–Polystyrene Graft Copolymers Formed by Gamma Irradiation, in *Abstracts of Papers, 138th National Meeting, American Chemical Society*, Sept. 11–16, 1960, New York, *Abstr.* 29, p. 12E.
32. R. Y.-M. Huang and W. H. Rapson, Grafting Polymers onto Cellulose by High Energy Radiation. II. Effect of Swelling Agents on the Gamma-Ray-Induced Direct Radiation Grafting of Styrene onto Cellulose, *J. Polymer Sci., Pt. C: Polymer Symposia*, No. 2, pp. 169-188 (1963).
33. A. Chapiro and V. Stannett, Direct Radiation Grafting onto Hydrophilic Polymers, *Intern J. Appl. Radiation Isotopes*, 8: 164-167 (1960).
34. Grafted Cellulose Doesn't Contain Much Grafted Polymer, *Chem. Eng. News*, 40(25): 57-59 (June 18, 1962).
35. H. Yasuda, J. A. Wray, and V. Stannett, Preparation and Characterization of Some Cellulose Graft Copolymers. I., *J. Polymer Sci., Pt. C: Polymer Symposia*, No. 2, pp. 387-402 (1963).
36. V. Stannett, J. D. Wellons, and H. Yasuda, Preparation and Characterization of Some Cellulose Graft Copolymers. II., *J. Polymer Sci., Pt. C: Polymer Symposia*, No. 4, pp. 551-562 (1964).
37. I. Sakurada and F. Kimura, Research on Graft Polymerization to Cotton in Annual Report of the Japanese Association for Radiation Research on Polymers, USAEC Report AEC-tr-6231, pp. 105-111, 1964; I. Sakurada, N. Okada, and N. Hatayama, Radiation Induced Graft Polymerization on Cellulose, 3. Gamma Induced Graft Polymerization of Styrene on Several Types of Cellulose, in Annual Report of the Japanese Association for Radiation Research on Polymers, USAEC Report AEC-tr-6316, pp. 84-88, 1964; I. Sakurada, N. Okada, F. Kimura, and N. Minegawa, 4. Graft Polymerization of Styrene on Pre-Irradiated Cellulose with Varying Fine Structure, in Annual Report of the Japanese Association for Radiation Research on Polymers, USAEC Report AEC-tr-6316, pp. 89-94, 1964; I. Sakurada, N. Okada, F. Kimura, and N. Minegawa, 5. Radiation Induced Graftings on Several Types of Cellulose, in Annual Report of the Japanese Association for Radiation Research on Polymers, USAEC Report AEC-tr-6316, pp. 95-99, 1964; I. Sakurada, N. Okada, and N. Hatakeyama, Radiation Induced Graft Polymerization on Cellulose, 6. Effect of Solvents on Graft Reactions on Several Types of Cellulose, in Annual Report of the Japanese Association for Radiation Research on Polymers, USAEC Report AEC-tr-6372, pp. 83-88, 1964.
38. S. Okamura, T. Iwasaki, Y. Kobayashi, and K. Hayashi, Gamma-Ray-Initiated Graft Copolymerization on the Surface of Nylon Fibers and in the Inner Layers of Cellulose Fibers, in *Large Radiation Sources in Industry*, Conference Proceedings, Warsaw, 1959, Vol. 1, pp. 459-470, International Atomic Energy Agency, Vienna, 1960 (STI/PUB/12).
39. F. A. Long and L. J. Thompson, Water-Induced Acceleration of the Diffusion of Organic Vapors in Polymers, *J. Polymer Sci.*, 14: 321-327 (1954).
40. Y. Hayashibe, 2. Graft Polymerization of Styrene to Viscose Rayon by Pre-Irradiation, in Annual Report of the Japanese Association for Radiation Research on Polymers, USAEC Report AEC-tr-6231, pp. 103-104, 1964.
41. V. L. Karpov, Y. M. Malinsky, V. I. Serenkov, R. S. Klimanova, and A. S. Freidin, Radiation Makes Better Woods and Copolymers, *Nucleonics*, 18(3): 88-90 (1960).
42. J. A. Kent, A. Winston, and W. R. Boyle, Preparation of Wood-Plastic Combinations Using Gamma Radiation To Induce Polymerization; Effects of Gamma Radiation on Wood, Annual Report, November 1, 1961–October 31, 1962, USAEC Report ORO-600, West Virginia University, Mar. 1, 1963.
43. J. A. Kent, A. Winston, and W. R. Boyle, Preparation of Wood-Plastic Combinations Using Gamma Radiation To Induce Polymerization, Interim Report, USAEC Report ORO-612, West Virginia University, Sept. 1, 1963.
44. J. A. Kent, A. Winston, W. R. Boyle, W. Loos, and J. E. Ayres, Preparation of Wood-Plastic Combinations Using Gamma Radiation To Induce Polymerization, Interim Report, USAEC Report ORO-628, West Virginia University, May 14, 1965.
45. D. S. Ballantine, Use of Gamma Radiation To Produce Wood-Plastic Combinations, *Isotopes Radiation Technol.*, 1(2): 189-195 (Winter 1963–1964).
46. A. J. Stamm, *Wood and Cellulose Science*, The Ronald Press Company, New York, 1964.
47. D. L. Kenaga, J. P. Fennessey, and V. T. Stannett, Radiation Grafting of Vinyl Monomers to Wood, *Forest Prod. J.*, 12(4): 161-168 (1962).
48. K. V. Ramalingam, Enhancement of Properties of Wood by Gamma-Induced Graft Polymerization, M.Sc. Thesis, McMaster University, 1961.
49. S. L. Ross, Wood-Polymer Combinations—Some Fundamental Considerations, M.Eng. Thesis, McMaster University, 1965.
50. J. W. Hodgins, G. N. Werezak, and S. L. Ross, A Versatile Radiation Source for Studying Gamma-Initiated Reactions, *Can. J. Chem. Eng.*, 43: 117-119 (1965).

Section

VI

Isotopes and Radiation Technology

Applications in Medicine

The development of tracer theory is important to the application of radiotracers to solving a wide variety of practical problems. Tracers have been most extensively used in the biomedical field, but the principles of their use can be applied equally in other sciences and in industry. In the following review some of the fundamental theoretical aspects of tracer use are presented with the hope that experimenters will gain some insight into how their tools really work. The combined efforts of theorists and experimenters alike will be required for continued advances in the theory and use of tracers.

Tracer Theory: A Review

By Per-Erik E. Bergner,* M. D.

The theory, methods, and problems of tracer applications are reviewed with emphasis on biomedicine, although many of the conclusions may be valid for other scientific fields and for industry. A brief historical review traces the development in the theory before and after the classic papers of the late 1940's and early 1950's which founded linear first-order compartment analysis. *The mathematics for general cases and the approach to some applications are outlined. Attempts are made to recognize basic problems rather than to give laboratory methods. The communications gap between theory and practice is discussed; several fundamental problems are described which require solutions before completely reliable methods can be developed.*

The purpose of this article is to give a survey of tracer theory, its past and present status. Emphasis will be on biomedical applications simply because this is my personal field of interest and, moreover, because tracer methods have been most extensively used in biomedical research. The principles developed there usually contain as special cases the methods developed in, for instance, industrial tracer applications.

The topic is at present somewhat controversial, and no common terminology has been developed; the situation reminds one of what has been a rule in thermodynamics, where different authors use different symbols for the same concept and the same symbol for different concepts. The symbols and concepts to be used here are introduced in subsections 1 and 2, and, in addition, a list of definitions is given in the appendix.

Owing to the broad character of the topic, only the general principles of the theory can be covered, and the particular examples chosen are merely intended as illustrations.

1. Basic Concepts

A tracer is a substance that traces some other substance, which in this article I shall refer to as mother substance. Hence there cannot be any tracer if there is no mother substance (i.e., if there is nothing to trace); as will be explained later, there are not only conceptual but also physical reasons for this. For instance, in an organism like the human body there is a daily uptake and a daily output of potassium ions ($^{39}K^+$, $^{40}K^+$, $^{41}K^+$); when a small amount of $^{42}K^+$ is injected as tracer, the naturally present potassium might be looked upon as mother substance.

Almost every interpretation of tracer data assumes steady state in the sense that not only does the uptake equal the output for mother substance, but the amount of mother substance is time independent everywhere in the system (organism). This terminology is not in exact agreement with the one adopted in irreversible

*Per-Erik E. Bergner is a research scientist at the Medical Division, Oak Ridge Institute of Nuclear Studies, an operating unit of Oak Ridge Associated Universities, Inc., Oak Ridge, Tenn., under contract with the U. S. Atomic Energy Commission.

thermodynamics,[1] and in a more precise terminology the term "perfect tracer system" has been introduced.[2] However, as the term "steady state" is so often used, I feel it appropriate in the present context.

2. Formulation of a Problem

Let S and E denote the system (organism) and its environment, respectively. By the compartment C we understand an arbitrary domain of S, i.e.,

$$C \subseteq S$$

which means that C might coincide with the system. For example, the red cells, nerve cells, and Kupffer cells of the liver are potassium compartments. In the whole-body potassium compartment, $C = S$. Thus a compartment is defined geometrically, chemically, or both.

In the following we shall always assume steady state. Figure VI-1 shows the general situation. In Fig. VI-1

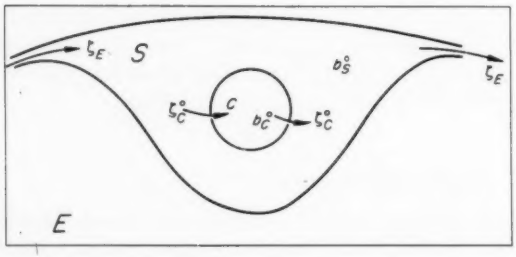


Fig. VI-1 General relation among system, environment, and compartment; $C \subseteq S \subset E$, and $b_C^\circ \subseteq b_S^\circ$.

S = the system (organism)
E = the environment of S
C = an arbitrary compartment in S
ζ_E° = the total flux of mother substance from E to S (number of particles/unit time)
ζ_C° = the total flux of mother substance to and from C (number of particles/unit time)
b_C° = the total amount of mother substance in C
b_S° = the total amount of mother substance in S

The superscript $^\circ$ refers to mother substance and denotes that the function is independent of time.

Assume now that at the time $t = 0$ a small amount of tracer is supplied to S. Let us further assume that there are experimental techniques* available so that, at each time $t > 0$, the total amounts of tracer $b_S(t)$ and $b_C(t)$ in S and C, respectively, can be observed. Figure VI-2 shows the general features of this type of data.

$b_S(t)$ = the total amount of tracer in S
$b_C(t)$ = the total amount of tracer in C

[Thus if x° denotes a time-independent entity of mother substance, $x(t)$ denotes the corresponding tracer entity at time t.]

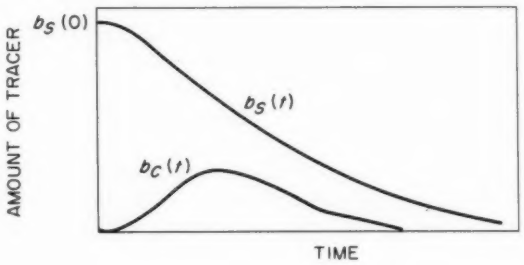


Fig. VI-2 Tracer curves from the whole system, $b_S(t)$, and from a compartment, $b_C(t)$.

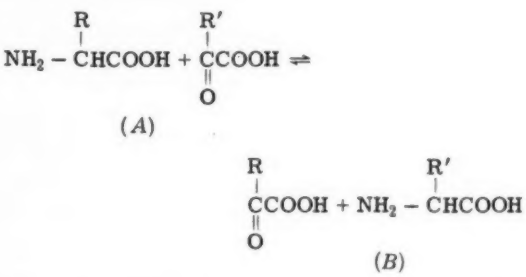
The purpose of a tracer experiment is made clear by the following problem. Given data of the type shown in Fig. VI-2, determine (i) b_S° and b_C°, sometimes referred to as pool sizes of S and C, respectively; (ii) ζ_E° and ζ_C°, sometimes referred to as the turnovers in S and C, respectively (especially ζ_E° is known as the whole-body turnover). To me this gives the general features of the basic problem in tracer methodology independent of any particular field of application, whether it be biology, clinical medicine, chemical industry, or geophysics.

3. Physical Dimensions

So that the entities in the previous subsection will have a physical meaning, we must sharpen their significance and confine it to particles; as

*"Experimental techniques" here include chemical and physical methods and depend on what substances are used. Thus, as radioisotopes are commonly used as tracers today, the experimental techniques usually consist of radioactivity measurements. The calibration (i.e., the conversion of "counts/min," say, into "moles") often causes problems; the conversion involves not only corrections for radioactive decay but also absorption and scattering of the emitted radiation, etc. Whereas a "whole-body curve" [$b_S(t)$, Fig. VI-2] often can be determined accurately, a compartment curve [$b_C(t)$, Fig. VI-2] frequently proves more difficult; see also subsection 6.

a matter of fact, we must go further and restrict it to atoms. The reason for this is because the concept of turnover will only be defined in terms of atoms for any arbitrary compartment. Thus the turnover is defined as flux, counted in number of particles leaving C per unit of time. Let us consider the transamination



(A) (B)

Here we cannot, without further specifications, speak of the flux of the amino acid A, say, from the left to the right. On the other hand, it makes sense to speak of the flux of nitrogen atoms from the left to the right,[3] and the two amino acids A and B might be considered as two different nitrogen compartments. Or, as pointed out by Stephenson,[4] label is conserved; in steady state, for example, the number of nitrogen-containing molecules entering S is not necessarily equal to the number of nitrogen-containing molecules leaving S, even though, on the other hand, the uptake of nitrogen atoms equals the output. Certainly there are several situations where the conservation condition is also satisfied for nonatomic particles, e.g., the red-blood-cell system discussed in subsection 8; but, if not specified otherwise, we shall in the following assume the b variables to have the dimension of gram atoms and the ξ variables to have the dimension gram atoms/unit of time. Usually the tracer atoms are radioactive, and experimental data are then primarily in the form of, say, counts per second. The conversion factors will be assumed to be well-known so that these data can be transformed into absolute numbers of atoms. That this introduces experimental difficulties is quite evident (see subsection 6).

4. Brief Historical Review

The idea of using some artificial substance as a tracer for physiological materials is neither very new nor confined to the use of radioisotopes; a classic example is the use of dyes in blood-circulation studies (see subsection 8). However, the development of radioisotope techniques has, especially since World War II, resulted in a rapid growth of what we today know as tracer kinetics.

The start was actually made just before and during the war by Schoenheimer[5] and Hevesy,[6] but their works were essentially concerned with the qualitative elucidation of metabolic pathways and not until the end of the 1940's did a quantitative kinetics begin to take shape.

Tracer curves as shown in Fig. VI-2 were soon recognized as the quite simple mathematical form

$$f(t) \equiv \sum_{l=1}^{l=n} \beta_l e^{-\alpha_l t} \qquad 0 \leq \alpha_1 < \alpha_2 < \cdots \qquad (1)$$

where the sets $\{\alpha_l\}$ and $\{\beta_l\}$ are time independent. Usually it was found that $n \leq 3$, and hardly ever was $n > 5$; as a natural consequence, people began making attempts to find rational explanations for these simple results.

First, equations for radioactive decay had been derived and solved by Bateman[7] as early as 1910, and Eq. 1 is identical with Bateman's general solution. An important point is that, in Bateman's function, each α_l is equal to the first-order rate constant of one reaction step; n is thus equal to the number of reaction steps between the original substance and the final product.

Second, in an attempt to analyze data from drug–kinetic experiments, Teorell[8] in 1937 had introduced the idea of considering the metabolic system as composed of a few well-stirred compartments between which the substance was exchanged according to first-order kinetics.

If there is any logic whatsoever in the historical process, a situation like this one can result in only one thing: n in Eq. 1 is interpreted as the number of reaction steps in which the tracer participates, and α_l's are the corresponding rate constants. However, this type of interpretation, which has been used, for example, in studies of calcium metabolism,[9] is valid only when the system consists of an unbranched chain of irreversible reaction steps,[10]

$$1 \rightarrow 2 \rightarrow 3 \rightarrow$$

or[11]

$$\leftarrow 4 \leftarrow 2 \leftarrow 1 \rightarrow 3 \rightarrow 5 \rightarrow$$

As soon as there is a branch

$$1 \rightarrow 2 \rightarrow 3 \begin{cases} \nearrow 4' \rightarrow 5' \rightarrow \\ \searrow 4 \rightarrow 5 \rightarrow \end{cases}$$

a reversible step

$$1 \rightarrow 2 \rightleftharpoons 3 \rightarrow 4 \rightarrow$$

or both, each α_l becomes, usually, a complicated function of all the reaction steps; this can be seen by applying classic chemical kinetics to the different kinds of reaction systems.[11]

Another form of tracer analysis, which also seems to be based on an analogy with radioactive decay, uses the fact that whole-body data [i.e., observed values of $b_S(t)$; see Fig. VI-3]

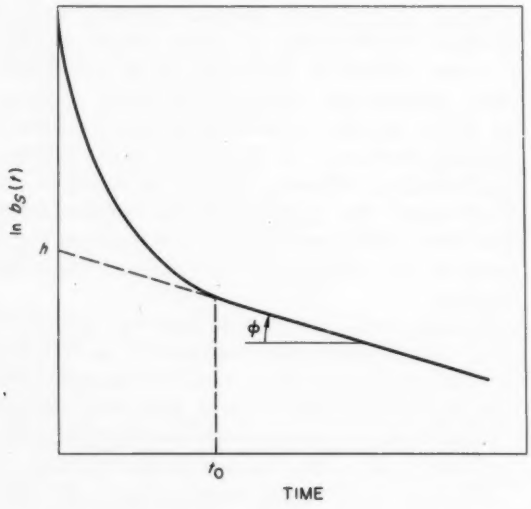


Fig. VI-3 Semilogarithmic plot of a whole-body-tracer curve with the last linear slope, ϕ, and the intercept, h, shown.

will be linear in a semilogarithmic plot for sufficiently large t values. In other words, after a sufficiently long time the tracer system will exhibit first-order kinetics, i.e.,

$$db_S(t)/dt \equiv \dot{b}_S(t) = -kb_S(t) \qquad t > t_0 \qquad (2)$$

Hence after the time t_0, the system will behave similarly to the "well-stirred" system shown in Fig. VI-4, where we assume a constant input ζ_E°

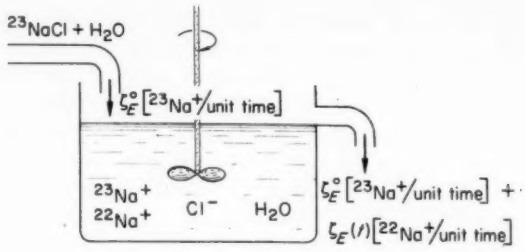


Fig. VI-4 A "well-stirred" tracer system.

(and equal output) of an aqueous NaCl solution. At the time $t = 0$, a small amount of ^{22}NaCl is added to the vessel. If the stirring is sufficiently good, the flux of tracer (i.e., number of $^{22}Na^+$ leaving S per unit of time) is

$$\zeta_E(t) = \zeta_E^\circ b_S(t)/b_S^\circ = -\dot{b}_S(t)$$

On the basis of such an analogy, the linear slope ϕ and the intercept h in Fig. VI-3 determine ζ_E° and b_S° (the turnover and the total pool size).

The frequently observed phenomenon that ln $b_S(t)$ becomes linear for large values of t has thus been interpreted as what is often referred to today as isotopic equilibrium: the proportion of tracer per unit amount of mother substance is the same everywhere in S when $t > t_0$. Among all ideas about tracer kinetics that have ever been born, isotopic equilibrium is one of the most fundamental and commonly accepted. The terminology reflects the analogy with the well-stirred system; the final linear slope is said to determine the biological half-life. The still-common clinical use of this term and, in general, the described use of final linear slopes and intercepts can be seen in the book *Dynamic Clinical Studies with Radioisotopes.*[12] We know today, however, that the idea of isotopic equilibrium in most biological situations is incorrect physically and, at best, approximate experimentally; but until recently no method for estimating the degree of approximation has been available (see, further, subsection 9).

Simultaneously with what one could call the intuitive methods of tracer analysis that I have discussed, other methods have been developed. An important event was the publication by Sheppard and Householder[13] of their classic paper in 1951. Experimental and theoretical works[14–16]

indicating the beginning of a new way of thinking had been published at the end of the 1940's, but the paper by Sheppard and Householder was the first successful attempt at a formal treatment of the subject as a whole; this paper still plays a central role and appears frequently in reference lists. The problem discussed there was: given a system consisting of a finite number of well-stirred (homogeneous) compartments between which there are first-order flows, what observations are necessary to determine these flows, and how will the system behave? Another problem discussed there concerns the so-called "lumping phenomenon" (see subsection 7).

The paper by Sheppard and Householder founded a general method, which is usually referred to as compartment analysis; in an attempt to make the language more precise, I shall, however, here refer to it as *linear first-order compartment analysis*, or LFCA. An important step in the further development of this method was made when Berman and Schoenfeld[17] in 1956 published a paper dealing with the following problem: if a linear compartment model and a set of data are given for a metabolic system, to what extent are the model parameters determined?

Methods of LFCA had been considered earlier in medicine as well as in industrial work (the equations for a set of equal and mixing containers in series are derived and solved in Ref. 18), and, after World War II, LFCA gradually developed into a specialized discipline of its own, which has had a considerable impact on many people's ways of thinking. Although doubts have been raised about the usefulness of LFCA and its physical significance,[10,19] and attempts at alternative methods have been made (see, further, subsection 8), LFCA is without question the most commonly used method today for analysis of tracer data.

5. The LFCA Method

Let C_i denote compartment i; that is, C_i is a domain of the total system S such that it defines uniquely an amount b_i° of mother substance. In other words, C_i is an entity defined morphologically or chemically, or both. We consider S subdivided into a set of N mutually exclusive compartments

$$b_S^\circ = \sum_{i=1}^{i=N} b_i^\circ$$

Consider then an amount $b_i(t)$ of tracer in C_i at time t, and let $\zeta_{ji}(t)$ denote the total flux (gram atoms/unit time) of tracer at the time t from C_i to C_j. If, with a constant λ_{ji}

$$\zeta_{ji}(t) = \lambda_{ji} b_i(t) \qquad j = 1, 2, \ldots, N \qquad j \neq i$$

is true for all values of t, we shall say that C_i is homogeneous and denote it by H_i. Many authors use the term compartment as a synonym for my term homogeneous compartment (e.g., Ref. 20, which gives one of the few serious attempts in the literature to define the compartment concept).

We assume now that all C_i's are homogeneous (i.e., $C_i = H_i$, $i = 1, 2, \ldots, N$) and that, for $t > 0$, there is no input of tracer into S:

$$\frac{db_i(t)}{dt} \equiv \dot{b}_i(t) = \sum_{\substack{j=1 \\ j\neq i}}^{j=N} \zeta_{ij}(t) - \sum_{\substack{j=1 \\ j\neq i}}^{j=N} \zeta_{ji}(t) - \zeta_{Ei}(t)$$

$$= \sum_{\substack{j=1 \\ j\neq i}}^{j=N} \lambda_{ij} b_j(t) - \lambda_{ii} b_i(t)$$

$$t > 0 \qquad i = 1, 2, \ldots, N \qquad \lambda_{ii} \geq 0$$

where $\zeta_{Ei}(t)$ is the tracer flux from H_i to the environment E; according to the assumption that $C_i \equiv H_i$, this flux is proportional to $b_i(t)$, and the constant of proportionality* is included in λ_{ii} and, consequently, $\lambda_{ii} b_i(t)$ is the total flux from H_i to other compartments as well as to the environment. The tracer process is thus described by a system of linear first-order differential equations, which usually is written in matrix notation

$$\dot{\bar{b}}(t) = \{\lambda_{ij}\}\, \bar{b}(t) \tag{3}$$

where $\bar{b}(t)$ denotes the column vector $\begin{pmatrix} b_1(t) \\ \vdots \\ b_N(t) \end{pmatrix}$

A physically detailed derivation of Eq. 3 is given in Ref. 21; one consequence of the underlying postulates is

*The notation ii is motivated by matrix notation to account for the diagonal. Of course, flux from C_i to C_i has no physical meaning.

$$\zeta^{\circ}_{ij} = \lambda_{ij} b^{\circ}_{j} \qquad i \neq j \qquad \left.\begin{matrix} i \\ j \end{matrix}\right\} = 1, 2, \ldots, N \qquad (4)$$

where ζ°_{ij} is the flux of mother substance from H_j to H_i. As we always assume stationarity, all quantities of mother substance as well as λ_{ij} are time independent. Thus, if we introduce the specific activity in H_i

$$a_i(t) \equiv b_i(t)/b^{\circ}_{i} \qquad i = 1, 2, \ldots, N \qquad (5)$$

Eq. 3 can be rewritten as

$$\dot{\bar{b}}(t) = \{\zeta^{\circ}_{ij}\}\, \bar{a}(t) \qquad (6)$$

where $\bar{a}(t)$ is the column vector $\begin{pmatrix} a_1(t) \\ \vdots \\ a_N(t) \end{pmatrix}$

The solution of Eq. 3 has long been known in mathematics and can be found in standard textbooks.[22] However, although the essential parts of the theory are well-known to mathematicians, its application to LFCA has obviously helped in the understanding of this theory by experimenters. Noteworthy here are the works by Sheppard and Householder,[13] Hearon,[23] Berman and Schoenfeld,[17] Rescigno,[24] and Matthews.[25] In addition to this, I do feel that these investigations, though perhaps not having contributed much to the world of mathematics, have put the spotlight on some of those parts of the theory of matrices and differential equations that are of special interest in physical applications. Thus the concepts of open vs. closed systems imply, under certain conditions, some restrictions[2,26] on the rank of $\{\lambda_{ij}\}$. The classic principle of conservation of mass has an equivalent in the conservation of probability, which also implies additional restrictions[2] on $\{\lambda_{ij}\}$.

In the consideration of conservation principles, the principle of detailed balance has received special attention in the literature. The origin of this interest is obviously thermodynamic,[1,27] although application of the principle to tracer systems might be doubted.[2] The principle of detailed balance states that in Eq. 6 the matrix $\{\zeta^{\circ}_{ij}\}$ is symmetrical, i.e., $\zeta^{\circ}_{ij} = \zeta^{\circ}_{ji}$, and though this principle is necessarily satisfied when a thermodynamically isolated system is in thermodynamic equilibrium,[1,27] it does not seem to be a necessary condition for the open system in steady state.

To the best of my knowledge, Jost[28] was the first (1947) to consider the mathematical consequences of detailed balance, and a few years later Hearon[23] published a more detailed analysis of a mathematically similar topic. We first notice that, if we apply only the principle of conservation of masses, the solution of Eq. 3 becomes (see, e.g., Ref. 2, Theorem 3)

$$b_i(t) = \sum_{l=1}^{l=n<N} \beta_{il}\, e^{-\alpha_l t}$$

$$t > 0 \qquad 0 \leq \alpha_1 \leq \alpha_2 \leq \text{---} \leq \alpha_n$$

and

$$\beta_{il} = \sum_{j=1}^{j=n} b_j(0)\eta_{ijl}$$

where $\eta_{ijl} = M_{ijl}(t) \cos u_l t + N_{ijl}(t) \sin u_l t$, with $u_l > 0$ only if $\alpha_l > 0$; here u_l and α_l are algebraic functions of $\{\lambda_{ij}\}$, and $M_{ijl}(t)$ and $N_{ijl}(t)$ are polynomials in t of degree $h_l - 1 \left(\sum_{l=1}^{l=n} h_l = N\right)$, the coefficients of which are algebraic functions of $\{\lambda_{ij}\}$. Although the case $h_l > 1$ is physically pathologic (this was pointed out to me by U. Uhlhorn in 1962), the fact that the general solution contains trigonometric functions is significant; as shown by Jost[28] and Hearon,[23] the principle of detailed balance implies that $u_l = 0$ for all values of l. In other words, the principle of detailed balance implies that the tracer process is nonperiodic.

It should be recalled that the discussion concerns the tracer process for nonnegative t values only and assumes that there is no tracer supply to S after $t = 0$. In what follows we shall continue to assume this condition (see Ref. 2 for the case when there is a prolonged tracer supply).

To sum up then, what has been said so far in the present subsection justifies the following statement: data that can be described in the form given by Eq. 1 are mathematically consistent with the hypothesis that the system S consists of (or can be considered as consisting of) a finite number of homogeneous compartments. This is the basis of LFCA, which is applied in essentially two ways:

(*a*) In terms of some rules of statistics and error analysis, the best-fitting expressions of the form Eq. 1 are determined for a given set of data. By inspection of the functions thus derived, one then tries to construct the simplest possible and physicobiologically most sensible linear compartment model. The β and α values are used to determine $\{\lambda_{ij}\}$.

(*b*) On the basis of physicobiological arguments, one constructs a linear compartment model. The resulting $\{\lambda_{ij}\}$ is then determined by some method so that the model as well as possible (in some sense) fits the given set of data.

Often (*a*) and (*b*) are used simultaneously; one starts with a model and modifies it after tentative curve fittings. However, for several reasons (*a*) is hardly acceptable; among other things, such an approach makes it conceptually impossible to discuss experimental errors, and the resulting model could reflect those errors as much as the underlying physiology.

Whereas Sheppard and Householder[13] discussed the problems associated with a physical system consisting of a finite number of homogeneous compartments, Berman and Schoenfeld[17] were, to the best of my knowledge, the first ones to introduce the concept of an a priori model into tracer theory and to give an analysis of the degree to which such a model is uniquely determined by given sets of data. In other words, the more physically oriented analysis of Sheppard and Householder was replaced by Berman and Schoenfeld with a rational formalism. The step made by the latter workers was bold and creative, and it gave tracer thinking a new direction.

The basic principles of the method are as follows: One starts with a given model and solves the corresponding differential equations. The solutions, which are of the form of Eq. 1 (i.e., all β_l's are assumed to be time independent), are then fitted to available data. Berman and Schoenfeld gave a general method for using the consequently determined α and β values for estimating $\{\lambda_{ij}\}$ or, for incomplete data, the restrictions imposed on the matrix.

Thus:

$$\text{Given model} \rightarrow \{\lambda_{ij}\} \rightarrow b_i(t) = \sum_{l=1}^{l=N} \beta_{il} e^{-\alpha_l t} \qquad i = 1, \ldots, N$$

→ given data + curve fitting → some α_l and β_{il} are given numerical values → some constraints on $\{\lambda_{ij}\}$.

The uniqueness of the constraints on $\{\lambda_{ij}\}$ is a conceptually and mathematically nontrivial problem,[29,30] and, so far as I know, no satisfactory solution has hitherto been presented. Moreover, the assumption that all β_{il}'s are time independent imposes physically unmotivated restrictions on the model (e.g., Chap. 4 in Ref. 10). This last objection has, it seems, been satisfactorily met by new numerical methods developed by Berman and others.[31,32] Instead of solving the differential equations for $\{\lambda_{ij}\}$, a computer determines $\{\lambda_{ij}\}$ directly by iterative methods. This gives the research worker a much larger degree of mathematical freedom in the choice of model. However, the problem of uniqueness seems still to exist. One possible definition of "unique model" would, of course, be that the computer procedure converges to a definite set of λ_{ij} values. But this is no proof of uniqueness in a physicomathematical sense, although it seems today accepted as such when nothing better is available, especially among workers in numerical analysis.

It is possible that the analysis might not lead to a unique model even in this sense, but leave one instead with several mathematically equivalent models. To solve this problem, Berman[33] introduced a "postulate": the model of choice is the one which is least sensitive to certain perturbations. So far as I can see, however, this is not a postulate in the sense usually used in theoretical science (see page 52 in Ref. 34), but rather a rule introduced to guarantee a unique representation of data. On the other hand, this indicates another aspect of the LFCA method: instead of speaking of a linear compartment model," one should perhaps consider the method as a way of constructing a "representation" of data. This question will be dealt with later.

Finally, it should be clearly understood that the purpose of determining $\{\lambda_{ij}\}$ is to solve a problem equivalent to the one formulated in subsection 2; the difference is that LFCA attacks a more complicated problem, i.e., it aims at a more detailed description of the system. Thus, if $\{\lambda_{ij}\}$ is known, the sizes $\{b_i^\circ\}$ and the fluxes $\{\xi_{ij}^\circ\}$ are essentially described.

6. Examples

In an article on the thyroid system, Berman[35] has given a clear description of an application of LFCA. A known amount of radioiodide is injected into a person, and one observes the radioactivity in plasma, plasma protein, the thyroid, and urine as a function of time. A simple model (Fig. VI-5) is used to begin with. However, the model contains not only the pa-

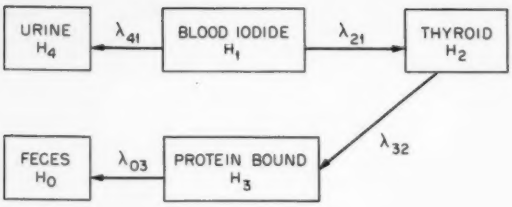


Fig. VI-5 A linear compartment model of iodine metabolism.[35]

rameters $\{\lambda_{ij}\}$ but also a set of proportionality constants $\{k_i\}$; in practice the total amount $b_i(t)$ of tracer in H_i cannot usually be observed, but rather a quantity $k_i b_i(t)$ proportional to the total amount, where k_i is unknown. Consequently the values of $\{\lambda_{ij}\}$ determined by fitting the model to data depend not only on the assumed physiology but also, in an uncertain way, on the experimental procedure, and so far as I understand, this must necessarily obscure the physiological significance of the numerical values of the model parameters $\{\lambda_{ij}\}$.

But this might not be too serious. If, instead of looking at the model as describing the physiological mechanism, we consider it as a way of representing data and accept or reject it in the same way as we accept or reject a coordinate system, depending on whether or not it is convenient for some purposes, then the approach seems quite adequate. This viewpoint is actually supported by Berman, who states that the original model (representation) shown in Fig. VI-5 has to be gradually modified (usually by subdividing the original compartments or by adding new compartments) so that it gives a satisfactory fit to all the different sets of data (patients) to which it is applied. When a representation with these mathematical properties is finally arrived at, its acceptance is eventually determined by whether or not it possesses properties that make pathophysiological sense to the clinician.

As the curve fitting is nonlinear, the least-squares method used might have several minima. The mathematical and methodological problems that this leads to are discussed in Ref. 35.

Berman thus uses an approach that is a mixture of conditions (*a*) and (*b*) described in subsection 5. In this respect the work by Garby et al.[36] differs in that they work exclusively according to (*b*); from this viewpoint I feel that the term "model" for their description of iron metabolism is adequate. These workers start with an a priori model (Fig. VI-6) based on the known physiology, and its structure is never modified during the investigation.

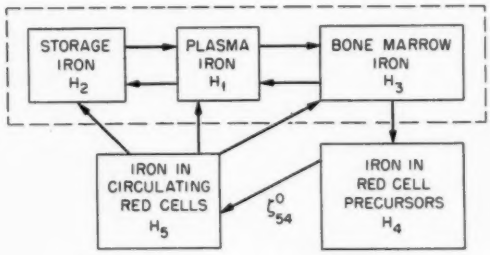


Fig. VI-6 The a priori compartment model for iron metabolism.[36]

Figure VI-6 is actually not a first-order linear compartment model in the usual sense. Only the part consisting of H_1, H_2, and H_3 can be considered as such, because the times the iron atoms have to spend in H_4 and H_5 have lower bounds; about 3 days in H_4 and 120 days in H_5. On the basis of specific assumptions for the fate of iron in H_4 and H_5, equations are derived for the appearance of radioiron in H_5 (assuming instantaneous supply of ^{59}Fe-labeled ferric citrate to H_1). These equations differ somewhat from the form of Eq. 1, whereas the equation for the disappearance of iron in H_1 (which is also observable) is of that form. Nevertheless, the equations contain a few parameters that are known a priori, and with the use of those values, the remaining, and unknown, parameters are determined by a least-squares fit to the data. These authors also discuss, as does Berman, the problem of the existence of several least-squares minima. However, this paper also states that the mathematically best-fitted model is not necessarily the one that makes most sense to the biologist, and, as a consequence, the authors use a somewhat more "manual" computer method where the operator (experimenter) can interact during the fitting process.

The reason for the authors' being skeptical of the best fit is simply that, as they point out, the assumption of homogeneity within the compartments is nontrivial. Hence, although the model seems to predict a reasonable value of the flux ζ^0_{54} (which essentially is the red-cell production and can be determined by indepen-

dent means), this does not guarantee that the values the model gives for nonobservable quantities of H_2, H_3, and H_4 are correct; the reason for this will be discussed in the next subsection.

Compared to Berman's approach, the one of Garby et al. is less general. An even more specific approach, which has little in common with the LFCA method, has recently been presented by Bernard, Uppuluri, and Shenton[37] for the analysis of strontium data. When a bone-seeking radio-ion like $^{90}Sr^{2+}$ is injected into the bloodstream, it accumulates at certain positions in the bone (these can be seen as "hot spots" on autoradiographs); this is because the osteoblasts are nonuniformly distributed in the bone tissue and seem to be active in discrete time intervals only. The model proposed by Bernard, Uppuluri, and Shenton is shown in Fig. VI-7.

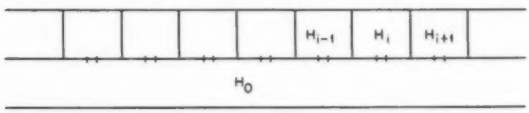


Fig. VI-7 A stochastic compartment model.[37] The connections between H_i and H_0 can be opened or closed (see text).

We consider a system consisting of the vascular blood compartment H_0, to which there are connected a large number of compartments $\{H_i\}$ and between which there are no interconnections. The connection between H_0 and H_i may be open or closed; when it is open there is an exchange of $^{90}Sr^{2+}$ between the two compartments according to first-order kinetics, the time of opening being subject to some ascribed probability distribution. A kind of many-parameter stochastic system, which is of interest not only from the viewpoint of stochastic theory but also from the viewpoint of linear compartment analysis, is the result. The functions the authors derive for the concentration of $^{90}Sr^{2+}$ in blood have a striking similarity, formally, with those that LFCA usually leads to.

This analysis deals with a quite confined, specific physiological process, and consequently the model also becomes specific. As a general rule the more specific and well-defined the studied mechanism is, the more confidence there is in the physical significance of the theoretical analysis (the model).

Other examples of these more specific physicochemical analyses are studies of enzymatic exchange reactions[38] and evaluations of the kinetics of metabolic breakdowns of complicated molecules where it might be profitable to use tracer molecules containing more than one radioisotope;[39,40] the different parts of a complicated metabolite undergo, simultaneously, different physicochemical transformations. For a further discussion of the application of tracers in enzyme and metabolic kinetics, the reader may consult Ref. 11; the following will be essentially confined to the more general aspects of tracer theory.

7. On the Physical Significance of LFCA

The two main difficulties with LFCA theory are, I think, the following: (A) It does not provide any physical definition of homogeneous compartment, and (B) it does not in itself provide any physical justification of why the tracer kinetics should be linear. The definition of homogeneous compartment given in Ref. 20 is operational (see the beginning of subsection 5), not microphysical.

Let us start with the physically most precisely described *state* of an atom. We denote this state by the vector $\bar{q}$, which spans the *state space* Q. The system S (the organism) as well as the compartment C may then be considered as sets of states ($C \subseteq S \subset Q$). One possible definition of homogeneous compartment is then immediately given by classical physicochemical kinetics. In a chemical reaction $M \rightleftharpoons N$, each compound (M,N) is considered as a homogeneous compartment in the sense that the assembly of molecules is assumed to be in thermal equilibrium, i.e., the energy distribution is given by Boltzmann's distribution law. This assumption seems to be reasonable, except for extremely rapid reactions.[1]

Clearly this definition is not applicable to metabolic kinetics; even if each compartment consists of the same kind of molecules, there is at least a spatial distribution. On the other hand, we might interpret the foregoing physicochemical concept of homogeneity as rapid stirring; the mixing within a compartment C is rapid enough to cause a kind of equilibrium throughout the reaction, i.e., the normalized distribution of atoms over the different $\bar{q}$ states in C is time independent (see Theorem 2 in Ref. 21). I shall refer to this as *mixing homogeneity*.

Another possible kind of homogeneity of a compartment C occurs when the probability that an atom in C will leave C is equal for all $\bar{q}$ states in C (see Theorem 2 in Ref. 21). In other words, the different states in C are in a certain way lumped together, and, as shown by Sheppard and Householder,[13] under certain circumstances such a lumping might be extremely efficient. In this discussion it is sufficient that the different states are almost equal. I shall refer to this as *lumping homogeneity*.

Mixing and lumping are likely to be extensive in an organism, which therefore might be described in terms of a finite number of homogeneous compartments. However, even if this is true, we are left with another problem: If a system S consists of a finite number of homogeneous compartments and if the tracer kinetics are linear, the number of exponential terms necessary to describe the tracer process in a compartment is likely to decrease as the time scale used in the observations[10] increases linearly. In other words, an increase in observational time scale is likely to result in a simplified phenomenological behavior of the tracer, i.e., S behaves as if it consists of a fewer number of homogeneous compartments than it really does. I shall refer to this phenomenon as *time-scale lumping*.

To sum up then, the phenomenological behavior of a tracer process as expressed in a linear compartment model depends on (1) mixing homogeneity, (2) lumping homogeneity, and (3) time-scale lumping. All three factors seem to work in the same direction, causing complicated systems to behave rather simply. Thus it is no wonder that complicated systems can often be described in the form of rather simple LFCA models. However, whereas (1) and (2) are phenomena that would hardly cause much difficulty in regard to the physical significance of an LFCA model, (3) definitely does. Namely, some homogeneity properties of S [partly equivalent to (1) and (2)] seem to be independent of time scale. In other words, whereas the LFCA model is partly dependent, in an uncertain way, on the time scale of observation, there appear to be physical properties of S that are independent of time scale but at the same time important for the model's significance.

We are, it seems, left with a basic inconsistency of tracer theory, which introduces problems that, so far as I know, have not yet been solved. The problems are of obvious interest also outside tracer theory, e.g., in certain types of relaxation methods where similar techniques are used.[41]

The physical justification of linearity [cf. condition (B) above] does not introduce any serious theoretical problem; it requires only some caution that might introduce experimental difficulties. Thus all that is necessary is to assume the presence of a mother substance in steady state. For further details on this point, the reader is referred to Ref. 21; I here merely want to emphasize that, as indicated in subsection 1, the concept of mother substance is physically necessary. As will be shown in the next subsection, it is also conceptually necessary. Moreover, here also we have a connection between tracer and relaxation theory; in relaxation studies one usually starts with a system in equilibrium, and linearity with respect to small perturbations is then easily justified provided the system can be assumed functionally continuous.[41] In tracer studies of open systems, equilibrium condition in relaxation theory is replaced by steady state.

Finally, there is an additional problem, almost completely neglected in the literature: the tracer process is dependent on how the tracer is supplied to the system. By writing the general solution to Eq. 3 in the form of eigenvectors[42] to $\{\lambda_{ij}\}$, it is easily seen that one can theoretically always get a system S to behave as a well-mixed system according to Fig. VI-4 (this was recently pointed out to me by J. D. Lawson, Waterloo, Canada).

8. Other Forms of Tracer Analysis

One possibility for solving some of the problems listed in subsection 7 is to start with the assumption that the system S consists of a finite but unknown number of homogeneous compartments $\{H_i\}$ and see what questions can be answered when the topological structure of S is unknown. An analysis along those lines has been done by B. Nosslin (so far as I know he has not published it himself, but in Ref. 43 his work is presented as an appendix; see also Ref. 44). Nosslin's results agree essentially with those to be presented later in this section.

Another possibility is to show, as done for instance by Sheppard,[45] that the calculations are insensitive to reasonable heterogeneity (see also Donato et al.[46]), but apparently the results are not yet conclusive, partly because the concept of homogeneity still lacks a physi-

cally precise definition. The same seems to be true for the work done by Wrenshall,[47] Schachter,[48] and Wrenshall and Hetenyi.[49] However, those works represent the only serious attempts I know of to test the validity of the homogeneity assumption, which in tracer kinetics so often is made ad hoc. But whereas their results do not seem to make possible the formulation of general rules, they do indicate that certain metabolic fluxes can be determined by using simple two-compartment models where only the accessible compartment (e.g., the blood compartment in an animal) has to be homogeneous (cf. also Chap. 8 in Ref. 10).

A third possible approach is to avoid using the homogeneity concept at all. The first attempt in that direction seems to be represented by Branson's work[50] in 1946, in which the tracer process was described by an integral equation. A basic insufficiency in that work was discovered later,[51,52] however, and the technique has not been used until recently.[53,54] The results agree essentially with those discussed later; the question is merely one of different mathematical methods.

Surprisingly enough, one of the most general and most successful methods of tracer analysis has been developed in a rather specific field: determinations of volumes and fluxes of blood. Methods based on the use of a dye as indicator substance were presented as early as 1897 by Stewart[55] and further developed and used by Hamilton et al.[56] Consider an organ O, through which there is a total flux F of blood (see Fig. VI-8). At the arterial end Ar there is at

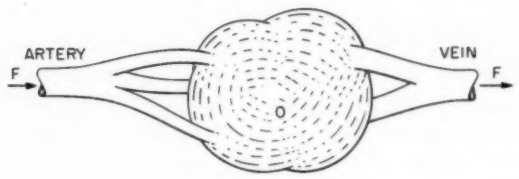


Fig. VI-8 Blood flow system.

the time $t = 0$ an injection of a small amount M of indicator substance I, and at the venous end Ve, one observes the concentration $c(t)$ of I as a function of time. What today are commonly referred to as the Stewart–Hamilton equations then take the form

$$M = F \int_0^\infty c(t)\, dt \qquad (7a)$$

$$V = \frac{F^2}{M} \int_0^\infty t\, c(t)\, dt \qquad (7b)$$

where V denotes the blood volume in the organism.

A formally satisfactory derivation of Eq. 7 was made in 1954 by Meier and Zierler,[57] who considered the tracer process in statistical terms (cf. also Refs. 45 and 58). Basically similar ideas were used a few years later by Andersson[59] for the derivation of equations for the cerebral blood system, where the problems are: (1) there is more than one vessel leading to and from the brain; and (2) the indicator substance (the tracer) has to be injected at a distance from the brain, implying that the tracer supply is no longer instantaneous.

The principles of Stewart–Hamilton's equations have been developed and used in fields other than biology and medicine, e.g., in geophysics[60,61] and industry.[62–64] The methods of Meier and Zierler focus attention on the fact that the particles do not spend an equal time in the system and lead to the idea of *residence time* distribution. This has been further developed by Zierler[65,66] (cf. also Zierler in Ref. 12) and by Sheppard,[67] who considers the problem in terms of parallel random walks. The problem of how long a time a particle will spend in a system is of obvious interest in the chemical industry, and similar work has been done there.[68–71] An analysis of linear compartment systems in such terms has been presented by Marsaglia.[72]

In these studies, except the one of Marsaglia, emphasis has been on fluid systems, and from this point of view the work by Stephenson[53] is of interest. Equations equivalent to Eq. 7 are derived there for an arbitrary S, and Stephenson concludes that the total pool size and the total turnover (cf. subsection 2) can thus be determined without making reference to any specific compartment model. However, I have hitherto used the terms "volume" (pool size) V and "flux" (turnover) F without specifying them physically. For example, the composition of blood is, as a principle, at Ar different from the composition at Ve (Fig. VI-8), a fact that immediately obscures the physical significance of V and F. Zierler[65,66] pays some attention to this by discussing the meaning of V [volume is there interpreted as the geometric domain traversed by a tracer particle (cf. also Ref. 12)]. But as the dynamic properties are

different for different kinds of tracer particles, this makes uncertain the exact physicobiological meaning of the entities F and V calculated from tracer data.

This problem is, however, not too serious; it can be solved in an almost trivial way. Let us start with a system S shown in Fig. VI-1, assuming steady state of mother substance. It can be shown[3,73] that, for an arbitrary compartment $C \subseteq S$, one has (subsections 1 and 2)

$$b_C(0) = \zeta_E^\circ \int_0^\infty \frac{b_C(t)}{b_C^\circ}\, dt \qquad (8)$$

But, as this is true also for $C = S$, one obtains

$$b_S(0) = \zeta_E^\circ \int_0^\infty \frac{b_S(t)}{b_S^\circ}\, dt \qquad (9)$$

where we can make the following identification with Eq. 7*a*:

$$b_S(0) = M$$

$$\zeta_E^\circ = F$$

$$b_S(t)/b_S^\circ = c(t)$$

It is thus possible to obtain both the Stewart–Hamilton equations as a special case ($C = S$) and, at the same time, a detailed physical meaning of the entities that appear in those equations. Thus the flux F becomes ζ_E°, the flux of mother substance (number of particles per unit of time), and in addition, $b_S^\circ = V$, i.e., we get volume as the total amount of mother substance (total number of particles) in S (the organ O). Thus if we use labeled red cells as tracer, volume is the total number of nonlabeled red cells in O, the organ, whereas if we use Evan's blue (a dye that is sorbed by certain types of gamma globulins), volume is the total number of such globulin molecules in the organ, although this interpretation depends on the uniformity of the dye-sorption process.

We have been able to solve some parts of the problem formulated in subsection 2, namely, how to determine b_S° and ζ_E° (see Ref. 44 for the experimental techniques as well as for further details concerning the meaning of b_S°, the exchangeable mass). But we have not yet been able to obtain a general method for determination of b_C° and ζ_C° (see subsection 9). However, we have obtained an illustration of the important concept that, in a tracer experiment, a definite mother substance can be identified; in the absence of a mother substance, not only does the physical motivation of tracer analysis become obscure, but in addition, entities like volume and flux lose their exact significance.

9. Concluding Remarks

What are the physical mechanisms behind tracer processes? Or, to be more specific, do tracers measure fluxes? Edwards and Harris[74] and Nims[75] have investigated these problems. However, the analyses consider rather detailed, specific physical systems and therefore do not provide general answers. One reason for this is that the overall tracer process observed in a metabolic system is the result of a conglomerate of different physicochemical processes that cannot be specified in detail; moreover, classic physical theory does not provide any tools for simultaneous treatment of scalar and vector fluxes (e.g., chemical reactions and diffusions).[1]

One possibility is suggested by relaxation theory;[41] we consider the tracer process in terms of small perturbations of an equilibrium system. Such an approach, explicitly indicated by Ackerman and Hazelrig,[32] has many attractive features but has the disadvantage of being too general microphysically. Another possibility is to construct a physical representation where, for example, the problem of scalars and vectors never occurs. This can be done,[21] where one then considers the movement of a tracer or mother substance particle as a time-homogeneous Markovian process in an abstract state space Q (see subsection 7). In this general theory the tracer is looked upon as a population of particles that is extremely diluted in a stationary phase of dynamically equivalent particles—the mother substance. The tracer process is here represented by a population of trajectories of individual particles through the Q space. The problem is to relate parameters describing this population of trajectories to parameters describing the steady-state distribution of mother substance.

In this approach, tracer theory comes out as a specific physical theory with certain similarities to classic statistical mechanics. Thus this kind of tracer dynamics leads to ergodic theorems showing that the whole tracer process (i.e., from $t = 0$ to $t = \infty$), and not isolated parts of it, represents mother substance.[44,73] This is the reason the type of analysis shown in Fig. VI-3 is not generally acceptable.

Consequently, instead of being confined to a specific experimental method with a limited field of applicability, tracer theory appears quite general. For example, the life span of an organism can be thought of as a trajectory through a state space, and the problem then is to what extent observations of an organism can be used for the description of the population to which it belongs (mother substance). In other words, general tracer dynamics might be of interest not only in the study of elementary physicochemical processes as they appear in enzyme kinetics, metabolism, and chemical industry, but also in the study of "higher" processes like cell-population dynamics, ecology, and (why not?) sociology.

Equations 8 and 9 can be derived from this kind of general theory, which gives them a quite general and precise significance; for example, they may be used as standard references for estimating errors in the experimentally simpler methods[44] described in subsection 4 (cf. Fig. VI-3). However, criticism against this physically more precise tracer theory can easily be formulated. First of all, many of the results that the theory has hitherto given are seemingly negative. Although it has provided us with a general answer of how to determine the total pool size b_S° and the total turnover ζ_E°, the theory has failed to give methods for determination of b_C° and ζ_C° of an arbitrary compartment C. As a matter of fact, in the general case, ζ_C° is a nondeterminable entity. Thus at present we can give an exact and physiologically meaningful interpretation only of the integral of the whole-body curve $b_S(t)$ in Fig. VI-3, and we have no physical theory that provides us with tools for an analysis of the compartment curve $b_C(t)$. This becomes even more definite when, as discussed at the beginning of subsection 6, we cannot observe $b_C(t)$ but only a quantity proportional to that variable, where then the constant of proportionality is unknown.

It seems to me that many experimenters feel that the physical tracer theory merely prevents them from doing things they think are possible. In practical work what is often needed is an analysis that makes sense to the experimenter (the doctor or the engineer), and usually he could not care less about microphysical significance. From this point of view, LFCA appears much more flexible and practical; especially in the form Berman and others have given to it, the method seems to allow for an almost unlimited amount of knowledge and experience to be incorporated in a uniform representation.

There is, however, no reason for considering the different approaches as being opposed to each other; rather, they complement each other. Their successes and failures are in different domains, and to believe that sooner or later they will converge toward a unified theory does not seem too optimistic. Meanwhile, it is recommended that the experimenter use the theory he feels best corresponds to the purpose of his particular work, and often practical success can be achieved without the use of any "theory" at all. Thus, to conclude with a specific example, one of the most successful applications of tracer methodology in medicine is the use of radioiodine for diagnosis of malfunctions of the thyroid.[76] There, purely operational parameters (the relative uptake of radioiodine after 3 or 6 or 24 hr) have been correlated with other clinical variables, and the parameters have then been given a *clinical significance*; i.e., one can use them as diagnostic tools without having either to consider their physicobiological significance or to refer to any detailed compartment model.

For those readers who would like to dig deeper into the subject, I should like to emphasize Refs. 12, 45, and 64; Vol. 108 of the *Annals of the New York Academy of Science* (to which several specific references have been made here) contains many interesting articles that give a rather differentiated picture of the whole topic. A particular mathematical formalism for analysis of kinetic data (not only tracer) has been developed by Rescigno and Segre.[77] In the present article I have only considered steady-state systems; an attempt to analyze nonsteady-state systems has been presented by Hart.[78]

Appendix: Definitions of Some Common Concepts

The tracer literature is crowded with technical terms, many of which are difficult to accept formally. Some of these reflect the almost desperate attempts of different investigators to describe systems that are overwhelmingly complicated when considered in classic physical terms. The following list of definitions is by no means complete but may be of some help as

an illustration of the conceptual problems in today's tracer theory. No one definition should be taken too seriously. The definitions have by necessity received a personal touch and reflect what I feel are different authors' meanings of the terms. Some of them are my own. When applicable, the subsection is given in which the concept has been introduced in the preceding article; terms within quotation marks are defined elsewhere in the list.

Compartment. (Subsection 2) (1) An arbitrary domain of a studied system; the domain is sometimes conceptual, sometimes defined by the method of measurement (e.g., the domain *seen* by the detector at external counting of radioactivity). (2) For some investigators (especially those working with "LFCA") a compartment is a domain within which the "specific activity" is everywhere equal (a *well-stirred* compartment); the concept is often considered as an abstraction or as an idealized physical entity.

In compartmentalization, a system is mentally or experimentally divided into mutually exclusive "compartments" or "pools." A compartmentalized system results.

Equivalent tracer supply. The supply of "tracer" to a system (organism) is said to be equivalent when the tracer particles enter the system in the same way as the particles of "mother substance." Although the requirement of an equivalent tracer supply is often difficult to satisfy experimentally, it is theoretically a necessary condition for tracer data to be representative of the state of mother substance.

Exchangeable mass. (Subsection 8) That part of the whole-body "pool" with a sufficiently large "turnover" to influence tracer data.

Half-time, biological. (Subsection 4) Two definitions can be given. (1) Let $r = -\tan \phi$ where ϕ is the angle of the "last linear slope" in Fig. VI-3. By an analogy with physical half-time, biological half-time ($t_{\frac{1}{2}}$) is defined as $\ln 2/r$. (2) $t_{\frac{1}{2}}$ may also denote the time for 50% of the *originally present* material to disappear. For this concept, which is general and in no conflict with the physical one, I suggest the notation t_{50}.

Half-time, physical. In a first-order reaction, such as radioactive decay, the amount of original substance remaining at the time $t \geq 0$ is proportional to e^{-kt}, $k > 0$. The half-time, usually denoted by $t_{\frac{1}{2}}$, then equals $\ln 2/k$ and is the time for the amount of substance present at *any* time to decrease 50%.

Homogeneous compartment. (Subsection 5) A "compartment" in which all the effluxes of tracer are proportional to the compartment's total content of tracer at any instant during the tracer process. The well-stirred compartment, i.e., a compartment with uniform "specific activity," is one possible type of homogeneous compartment (cf. Subsection 7).

Indicator substance. (Subsection 8) A synonym for "tracer," this term is usually used for dyes employed in studies of fluid systems (e.g., the vascular blood compartment, rivers, and dams).

Isotope dilution. A method for determination of the "exchangeable mass" based on the assumption of "isotopic equilibrium." Commonly the intercept of the "last linear slope" is used: If in Fig. VI-3 the curve refers to the "specific activity" in an accessible "compartment" (blood, for instance), then h is claimed to determine this specific activity at $t = 0$ (the time of tracer supply) if there was instantaneous mixing, i.e., "isotopic equilibrium." The exchangeable mass b_S° is then given by

$$b_S^\circ = b_S(0)/a(0)$$

where $a(0)$ is the "specific activity" determined by the intercept and $b_S(0)$ is the total amount of "tracer" supplied to the system.

Isotopic equilibrium. (Subsection 4) A condition in which the "specific activity" is the same everywhere in the system (this condition can hardly ever be satisfied in any open system).

Last linear slope. (Subsection 4) When the logarithm of a tracer curve is plotted against time, the result commonly becomes linear for time values greater than a certain number (the "mixing time"). The slope of this linear section is the last linear slope, which is frequently used for determination of biological half-time.

LFCA. (Subsection 4) Linear First-Order Compartment Analysis. An analysis in which the physical system is compartmentalized and represented by a finite set of first-order linear differential equations with constant coefficients. In defining these coefficients, one usually assumes that all the compartments are homogeneous.

Lumping. (Subsection 7) A situation in which a set of physically different states ex-

hibits itself kinetically as a single state. This is basically a property of the set's internal structure and is only indirectly a consequence of the observation method.

Mean first-passage time. A common concept in theory of stochastic processes. In tracer theory, the *expected* length of time between the particle's entrance and exit in a "compartment." When the particle cannot reenter the compartment (e.g., when the compartment contains the whole system), the mean first-passage time equals the "mean time of sojourn."

Mean time of sojourn. The total time the particle is *expected* to spend in a "compartment" before leaving the system for good.

Metabolic balance. The state at which an organism's intake of "mother substance" equals its excretion.

Mixing time. The time it takes for the whole system (body) "retention curve" to become exponential (cf. "last linear slope" and Fig. VI-3, where t_0 corresponds to the mixing time).

Mother substance. (Subsection 1) The substance naturally present in the system and which the "tracer" is supposed to trace.

Pool. To some investigators "pool" is synonymous with "compartment," definition (1).

Pool size. (Subsection 2) The total content of "mother substance" in a "compartment" or "pool" (i.e., in units of grams or moles).

Rate constant. When kinetic processes are described by differential equations with constant coefficients, the coefficients (such as $\{\lambda_{ij}\}$ in Subsection 5) are commonly referred to as rate constants. A rate constant usually has phenomenologic significance only, but it might occasionally be given microphysical significance. The latter is the case for "homogeneous compartments," and then the physical meaning of rate constant becomes equivalent to that of "turnover factor."

Relative amount. To obtain this quantity, usually the total amount of "tracer" present in a "compartment" is divided by the amount of tracer initially present in, or supplied to, the system.

Relative turnover. This is calculated by dividing the "turnover" by the compartment's content of "mother substance" (the "pool size").

Residence time. A period that seems to be equivalent to the "mean first-passage time."

Retention curve. The function that gives the amount of "tracer" remaining in a system after time t.

Space. The volume occupied by the total amount of a substance in a system when diluted to the same concentration that it has in the blood (plasma); the dimension is usually liters.

Specific activity. (Subsection 5) This quantity is the amount of "tracer" divided by the corresponding amount of "mother substance" (i.e., $b_i(t)/b_i^\circ$). Some authors consider the ratio $b_i(t)/[b_i^\circ + b_i(t)]$; however, in most situations $b_i(t) \ll b_i^\circ$, i.e., the amount of tracer is always and everywhere in the system much less than the corresponding amount of mother substance, and the ambiguity in definition becomes numerically unimportant. Common dimensions are millimoles per mole, counts per minute per gram, and counts per minute per millimole.

Steady state. (Subsection 1) The condition in which the amount of "mother substance" is constant in time everywhere in the system.

Theoretical volume. (1) This concept has been introduced by some investigators who use "LFCA" but who do not believe that the sizes or "volumes" that this method ascribes to the different "compartments" are correct. (2) This term also is a synonym for "space."

Time-scale lumping. (Subsection 7) A situation in which the complexity of the system's behavior decreases as the experimental time-scale is increased.

Tracer. (Subsection 1) A substance that is introduced into a system for studying the properties of some other substance (the "mother substance") in the system; the basic assumption is that the observer but not the system can discriminate between the two substances and that the tracer does not perturb the state of "mother substance."

Turnover. (Subsection 2) The amount of "mother substance" that leaves the "compartment" per unit of time; here "compartment" definition (1) is used, i.e., the compartment may be the whole system.

Turnover factor. The mean exit probability of "mother substance" particles in the "compartment." The mean is taken with respect to the "steady state" distribution and is numerically equal to the "relative turnover."

Turnover rate. This term is usually a synonym for "turnover."

Turnover time. A quantity that, when multiplied by the "turnover," gives the compartment's content of "mother substance" (the "pool size"); it is numerically equal to the

inverse of "turnover factor" or of "relative turnover."

Uptake. The "relative amount" of "tracer" present in an organ at a certain time after the tracer is supplied to the system (body), e.g., the iodine uptake of the thyroid.

Volume. (Subsection 8) Two definitions are given: (1) Ordinary geometrical volume (in cm^3, for instance). (2) A synonym for "pool size" (in moles, for instance).

References

1. K. G. Denbigh, *The Thermodynamics of the Steady State*, Methuen & Co., Ltd., London, 1951.
2. P.-E. E. Bergner, Tracer Dynamics: II. The Limiting Properties of the Tracer System, *J. Theoret. Biol.*, 1: 359-381 (1961).
3. P.-E. E. Bergner, Tracer Dynamics and the Determination of Pool-Sizes and Turnover Factors in Metabolic Systems, *J. Theoret. Biol.*, 6: 137-158 (1964).
4. J. L. Stephenson, Theory of Transport in Linear Biological Systems: II. Multiflux Problems, *Bull. Math. Biophys.*, 22: 113-138 (1960).
5. R. Schoenheimer, *The Dynamic State of Body Constituents*, Harvard University Press, Cambridge, Mass., 1942.
6. G. Hevesy, *Radioactive Indicators; Their Application in Biochemistry, Animal Physiology, and Pathology*, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1948.
7. H. Bateman, Solution of a System of Differential Equations in the Theory of Radio-Active Transformations, *Proc. Cambridge Phil. Soc.*, 15: 423-427 (1910).
8. T. Teorell, Kinetics of Distribution of Substances Administered to the Body; I. The Extravascular Modes of Administration, *Arch. Intern. Pharmacodyn.*, 57: 205-225 (1937).
9. R. O. Thomas, T. A. Litovitz, M. I. Rubin, and C. F. Geschickter, Dynamics of Calcium Metabolism. Time Distribution of Intravenously Administered Radiocalcium, *Am. J. Physiol.*, 169: 568-575 (1952).
10. P.-E. E. Bergner, The Significance of Certain Tracer Kinetical Methods, Especially with Respect to the Tracer Dynamic Definition of Metabolic Turnover, *Acta Radiol., Suppl.* 210, 1962, 59 pp.
11. H. G. Bray and K. White, *Kinetics and Thermodynamics in Biochemistry*, Academic Press Inc., New York, 1957.
12. R. M. Kniseley and W. N. Tauxe (Eds.), *Dynamic Clinical Studies with Radioisotopes*, AEC Symposium Series No. 3 (TID-7678), Oak Ridge, Tenn., 1964.
13. C. W. Sheppard and A. S. Householder, The Mathematical Basis of the Interpretation of Tracer Experiments in Closed Steady-State Systems, *J. Appl. Phys.*, 22: 510-520 (1951).
14. A. K. Solomon, Equations for Tracer Experiments, *J. Clin. Invest.*, 28: 1297-1307 (1949).
15. C. W. Sheppard, The Theory of the Study of Transfers Within a Multi-Compartment System Using Isotopic Tracers, *J. Appl. Phys.*, 19: 70-76 (1948).
16. C. W. Sheppard and W. R. Martin, Cation Exchange Between Cells and Plasma of Mammalian Blood; I. Methods and Applications to Potassium Exchange in Human Blood, *J. Gen. Physiol.*, 33: 703-722 (1950).
17. M. Berman and R. Schoenfeld, Invariants in Experimental Data on Linear Kinetics and the Formulation of Models, *J. Appl. Phys.*, 27: 1361-1370 (1956).
18. R. B. MacMullin and M. Weber, Jr., Determining the Efficiency of Continuous Mixers and Reactors, *Chem. & Met. Eng.*, 42: 254-257 (1935).
19. K. L. Zierler, Basic Aspects of Kinetic Theory as Applied to Tracer-Distribution Studies, pp. 381-472, in *Dynamic Clinical Studies with Radioisotopes*, R. M. Kniseley and W. N. Tauxe (Eds.), AEC Symposium Series, No. 3 (TID-7678), Oak Ridge, Tenn., 1964.
20. M. Berman, M. F. Weiss, and E. Shahn, Some Formal Approaches to the Analysis of Kinetic Data in Terms of Linear Compartmental Systems, *Biophys. J.*, 2: 289-316 (1962).
21. P.-E. E. Bergner, Tracer Dynamics: I. A Tentative Approach and Definition of Fundamental Concepts, *J. Theoret. Biol.*, 1: 120-140 (1961).
22. R. P. Agnew, *Differential Equations*, McGraw-Hill Book Company, Inc., New York, 1942.
23. J. Z. Hearon, The Kinetics of Linear Systems with Special Reference to Periodic Reactions, *Bull. Math. Biophys.*, 15: 121-141 (1953).
24. A. Rescigno, A Contribution to the Theory of Tracer Methods. II., *Biochim. Biophys. Acta*, 21: 111-116 (1956).
25. C. M. E. Matthews, The Theory of Tracer Experiments with ^{131}I-Labelled Plasma Proteins, *Phys. Med. Biol.*, 2: 36-53 (1957).
26. J. Z. Hearon, Theorems on Linear Systems, *Ann. N. Y. Acad. Sci.*, 108: 36-68 (1963).
27. I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, Charles C Thomas, Publisher, Springfield, Ill., 1955.
28. W. Jost, Über den Ablauf zusammengesetzer chemischer Reaktionen; Systeme von Reaktionen I. Ordnung. *Z. Naturforsch.*, 2A: 159-163 (1947).
29. P.-E. E. Bergner, On the Solution of the Compartmentalized Tracer System, *Exptl. Cell Res.*, 20: 579-580 (1960).
30. M. Berman and R. L. Schoenfeld, A Note on Unique Models in Tracer Kinetics, *Exptl. Cell. Res.*, 20: 574-578 (1960).
31. M. Berman, E. Shahn, and M. F. Weiss, The Routine Fitting of Kinetic Data to Models: A Mathematical Formalism for Digital Computers, *Biophys. J.*, 2: 275-287 (1962).
32. E. Ackerman and J. B. Hazelrig, Computer Applications to the Evaluation of Dynamic Biological Processes, pp. 19-53, in *Dynamic Clinical Studies with Radioisotopes*, R. M. Kniseley and W. N. Tauxe (Eds.), AEC Symposium Series, No. 3 (TID-7678), Oak Ridge, Tenn., 1964.
33. M. Berman, A Postulate to Aid in Model Building, *J. Theoret. Biol.*, 4: 229-236 (1963).
34. L. C. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics with Applications to Chemistry*, McGraw-Hill Book Company, Inc., New York, 1935.
35. M. Berman, Application of Differential Equations to the Study of the Thyroid System, pp. 87-99, in

Mathematical Statistics and Probabilities, Jerzy Neyman (Ed.), Symposium Proceedings, Berkeley, Calif., 1960, University of California Press, Berkeley, Calif., 1961.

36. L. Garby, W. Schneider, O. Sundquist, and J.-C. Vuille, A Ferro-Erythrokinetic Model and Its Properties, *Acta Physiol. Scand., Suppl.* 216, 1963, 26 pp.
37. S. R. Bernard, V. R. Uppuluri, and L. R. Shenton, Stochastic Models for the Distribution of Radioactive Material in a Connected System of Compartments, USAEC Report ORNL-3809, Oak Ridge National Laboratory, June 1965.
38. J. T-F. Wong and C. S. Hanes, Isotopic Exchange at Equilibrium as a Criterion of Enzymatic Mechanisms, *Nature*, 203: 492-494 (1964).
39. E. Gurpide, J. Mann, and E. Sandberg, Determination of Kinetic Parameters in a Two-Pool System by Administration of One or More Tracers, *Biochemistry*, 3(9): 1250-1255 (1964).
40. E. Sandberg, E. Gurpide, and S. Lieberman, Quantitative Studies on the Metabolism of Dehydroisoandrosterone Sulfate, *Biochemistry*, 3(9): 1256-1267 (1964).
41. M. Eigen and L. de Maeyer, Relaxation Methods, in *Rates and Mechanisms of Reactions*, S. L. Friess, E. S. Lewis, and A. Weissberger (Eds.), pp. 895-1054, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1963.
42. E. W. Montroll and K. E. Shuler, The Application of the Theory of Stochastic Processes to Chemical Kinetics, pp. 361-399, in *Advances in Chemical Physics*, I. Prigogine (Ed.), Interscience Publishers, a division of John Wiley & Sons, New York, 1958.
43. S. B. Andersen, *Metabolism of Human Gamma Globulin (yss-globulin)*, F. A. Davis Company, Philadelphia, 1964.
44. P.-E. E. Bergner, Exchangeable Mass: Determination Without Assumption of Isotopic Equilibrium, *Science*, 150: 1048-1050 (1965).
45. C. W. Sheppard, *Basic Principles of the Tracer Method; Introduction to Mathematical Tracer Kinetics*, John Wiley & Sons, Inc., New York, 1962.
46. L. Donato, C. Giuntini, R. Bianchi, and A. Maseri, Quantitative Radiocardiography for the Measurement of Pulmonary Blood Volume, pp. 267-283, in *Dynamic Clinical Studies with Radioisotopes*, R. M. Kniseley and W. N. Tauxe (Eds.), AEC Symposium Series, No. 3 (TID-7678), Oak Ridge, Tenn., 1964.
47. G. A. Wrenshall, Working Basis for the Tracer Measurement of Transfer Rates of a Metabolic Factor in Biological Systems Containing Compartments Whose Contents Do Not Intermix Rapidly, *Can. J. Biochem. Physiol.*, 33: 909-925 (1955).
48. H. Schachter, Direct Versus Tracer Measurement of Transfer Rates in a Hydrodynamic System Containing a Compartment Whose Contents Do Not Intermix Rapidly, *Can. J. Biochem. Physiol.*, 33: 940-947 (1955).
49. G. A. Wrenshall and G. Hetenyi, Jr., Tests of the Validity of Tracer-Calculated Amounts and Transfer Rates of Substances in Blood Plasma of Living Animal Systems, *Ann. N. Y. Acad. Sci.*, 108: 259-272 (1963).
50. H. Branson, A Mathematical Description of Metabolizing Systems: I, *Bull. Math. Biophys.*, 8: 159-165 (1946).
51. J. Z. Hearon, A Note on the Integral-Equation Description of Metabolizing Systems, *Bull. Math. Biophys.*, 15: 269-276 (1953).
52. R. A. Wijsman, A Critical Investigation of the Integral Description of Metabolizing Systems, *Bull. Math. Biophys.*, 15: 261-268 (1953).
53. J. L. Stephenson, Theory of Transport in Linear Biological Systems: I. Fundamental Integral Equation, *Bull. Math. Biophys.*, 22: 1-17 (1960).
54. H. Branson, The Integral Equation Representation of Reactions in Compartment Systems, *Ann. N. Y. Acad. Sci.*, 108: 4-14 (1963).
55. G. N. Stewart, Researches on the Circulation Time and on the Influences Which Affect It: IV. The Output of the Heart, *J. Physiol. London*, 22: 159-183 (1897).
56. W. F. Hamilton, J. W. More, J. M. Kinsman, and R. G. Spurling, Studies on the Circulation: IV. Further Analysis of the Injection Method, and of Changes in Hemodynamics Under Physiological and Pathological Conditions, *Am. J. Physiol.*, 99: 534-551 (1932).
57. P. Meier and K. L. Zierler, On the Theory of the Indicator-Dilution Method for Measurement of Blood Flow and Volume, *J. Appl. Physiol.*, 6: 731-744 (1954).
58. H. Sherman, On the Theory of Indicator-Dilution Methods Under Varying Blood-Flow Conditions, *Bull. Math. Biophys.*, 22: 417-424 (1960).
59. B. J. Andersson, Studies on the Circulation in Organic Systems, with Application to Indicator Methods, *Trans. Roy. Inst. Technol., Stockholm*, 114: 1-19 (1957).
60. J. Joly, On a New Method of Gaging the Discharge of Rivers, *Sci. Proc. Roy. Dublin Soc.*, 16: 489-491 (1922).
61. V. F. Hess, On the Use of a Radioactive-Tracer Method in Measurements of Water, *Trans. Am. Geophys. Union*, 24: 587-593 (April 1943).
62. C. G. Clayton, The Measurement of Flow of Liquids and Gases Using Radioactive Isotopes, *J. Brit. Nucl. Energy Soc.*, 3: 252-268 (1964).
63. D. E. Hull, The Total-Count Technique: A New Principle in Flow Measurement, *Int. J. Appl. Radiation Isotopes*, 4: 1-15 (1958).
64. L. G. Erwall, H. G. Forsberg, and K. Ljunggren, *Industrial Isotope Techniques*, John Wiley & Sons, Inc., New York, 1964.
65. K. L. Zierler, Effect of Circulatory Beds on Tracer Experiments, or Noncompartmental Analysis, *Ann. N. Y. Acad. Sci.*, 108: 106-116 (1963).
66. K. L. Zierler, Basic Aspects of Kinetic Theory as Applied to Tracer-Distribution Studies, pp. 55-79, in *Dynamic Clinical Studies with Radioisotopes*, R. M. Kniseley and W. N. Tauxe (Eds.), AEC Symposium Series, No. 3 (TID-7678), Oak Ridge, Tenn., 1964.
67. C. W. Sheppard, Stochastic Models for Tracer Experiments in the Circulation: Parallel Random Walks, *J. Theoret. Biol.*, 2: 33-47 (1962).
68. P. V. Danckwerts, Continuous-Flow Systems. Distribution of Residence Times, *Chem. Eng. Sci.*, 2: 1-13 (1953).
69. A. Cholette and L. Cloutier, Mixing Efficiency Determination for Continuous Flow Systems, *Can. J. Chem. Eng.*, 37: 105-112 (1959).
70. J. C. R. Turner, Residence-Time Measurements

in Chemical Plant, *Brit. Chem. Eng.*, 9: 12-16 (1964).

71. P. Naor and R. Shinnar, Representation and Evaluation of Residence Time Distribution, *Ind. Eng. Chem., Fundamentals*, 2: 278-286 (1963).
72. G. Marsaglia, Stochastic Analysis of Multi-Compartment Systems, Report D1-82-0280, Boeing Scientific Laboratory, 1963.
73. P.-E. E. Bergner, Kinetic Theory: Some Aspects on the Study of Metabolic Processes, pp. 1-18, in *Dynamic Clinical Studies with Radioisotopes*, R. M. Kniseley and W. N. Tauxe (Eds.), AEC Symposium Series, No. 3 (TID-7678), Oak Ridge, Tenn., 1964.
74. C. Edwards and E. J. Harris, Do Tracers Measure Fluxes? *Nature*, 175: 262 (1955).
75. L. F. Nims, Membranes, Tagged Components, and Membrane Transfer Coefficients, *Yale J. Biol. Med.*, 31: 373-386 (1959).
76. C. A. Owen, *Diagnostic Radioisotopes*, pp. 85-95, Charles C Thomas, Springfield, Ill., 1959.
77. A. Rescigno and G. Segre, La Cinetica dei Farmaci e dei Traccianti Radioattivi, Edizione Universitare, Torino, Boringhieri, 1961. [*Drug and Tracer Kinetics* (English translation), Blaisdell Publishing Co., Inc., Waltham, Mass., 1966.]
78. H. E. Hart, An Integral Equation Formulation of Perturbation-Tracer Analysis, *Ann. N. Y. Acad. Sci.*, 108: 23-28 (1963).

Section

VII

Isotopes and Radiation Technology

Isotopes Around the World

In this section the activities of the Euratom complex concerned with radioisotopes are described. Both work in promoting industrial uses of isotopes and synthesis and uses of radioisotope-labeled materials are discussed. State-of-the-art reports on production and uses of radioisotopes in Yugoslavia and Australia are presented. West German radioisotope imports are compiled, and a recent catalog of stable isotopes from East Germany is reviewed.

Radioisotope Programs in Euratom

Although the major part of the European Atomic Energy Community's (Euratom) work relates to the use of nuclear energy for the production of electricity, this major emphasis has not overshadowed equally vital problems such as the use of radioisotopes, radiation, and labeled compounds in industry and science.[1] The two major activities of Euratom in the radioisotope field — Bureau Eurisotop projects on the industrial uses of isotopes and work in other parts of the Community on labeled compounds — are described below.

Bureau Eurisotop

Bureau Eurisotop's task[2] is to promote the use of radioisotopes and radiation in industry. To this end, suitable instruments, methods of use, and materials are developed through research and development contracts. By acquiring and disseminating technical knowledge, the Bureau encourages the practical applications of radioisotopes and radiation. It also studies and helps to improve the legal, economic, and psychological conditions associated with their use (e.g., risk coverage, regulations, and services provided by industry). Lastly, the Bureau assists in coordinating at Community level the activities originating within the member states with those undertaken by groups in non-Community countries.

CONTRACTS

The principal goal of contracts placed by Eurisotop is to solve numerous industrial difficulties associated with the use of radioisotopes, especially in the fields of instrumentation, activation analysis, and radiation processing technology. At present the Bureau has some 60 contracts in operation and is negotiating about 30 more involving 26 branches of industry, such as metallurgy (blast furnaces), undersea construction, and textiles.

INFORMATION AND DOCUMENTATION

The Bureau has a "specialist library," which at the moment contains about 1300 books and reports, 30 thousand reference cards, and 600 reprints and photostats.

Reports from the contractor program are generally published by the Information and Documentation Centre (CID) as Euratom reports. Sixteen publications have already appeared. In addition, the Bureau publishes monthly the *Nouvelles du Bureau Eurisotop* (News of Bureau Eurisotop) in the four Community languages — French, German, Dutch, and Italian. Each number contains brief news items affording a rapid survey of the Bureau's activities for the month and from 5 to 10 documentary notes describing new or revised contracts.

The aim of the *Cahiers d'Information du Bureau Eurisotop* (Information Booklets of Bureau Eurisotop) is to publicize the full range of

nuclear methods and techniques, while providing accurate information on individual aspects of the industrial uses of radioisotopes. The booklets that have already been published are reviewed at the end of this section.

The Bureau also makes available for interested groups "Working Papers," which contain many articles, reprints, and bibliographies on a given subject.

A film for engineers and technicians entitled "Radioelements in Industry," illustrating the use of radioisotopes (with both French and Dutch sound tracks), was recently completed, and the Bureau, in cooperation with industrial firms, has also developed a number of exhibits for use at technical meetings.

COORDINATION

In activities promoting the use of radioisotopes, the techniques employed in the various fields of use, e.g., industry, research, and medicine, should be coordinated. Where such coordination has been done by negotiation—usually by the use of research contracts—lower research costs, rational division of labor, and efficient implementation of research projects have resulted.

Working groups have been formed to investigate possible uses of radioisotopes in studying coastal-sand erosion, industrial- and river-water purity, and water distribution systems.

Working groups have also been appointed in the field of activation analysis to organize a network of analysis centers. An information service now being set up will assemble all existing documentation on the subject. Research is also in progress on the determination of oxygen in steel. Most of the world's laboratories have been invited to take part in this work.

The principal effort, however, has been in the textile sector.[3] A study organized by the Community has had the cooperation of over 300 major textile enterprises and some 40 radioisotope experts. Four volumes containing technical papers for the working groups, as well as a very detailed subject index and an information handbook, have been published for the use of the participants. This activity was completed in June 1965, at which time study reports were published, working meetings were arranged, and a development program was prepared.

Lastly, mention should be made of the negotiations on a project involving a ship equipped with irradiation devices, to be used for irradiation tests and demonstrations near the enterprises concerned.

LEGAL AND ECONOMIC ASPECTS OF THE USE OF RADIOISOTOPES

The Bureau has compiled a reference library of industries that supply goods and services needed in radioisotope applications (including 250 non-Community firms). It has drawn up a list of the services that can be provided by industry and has started on a series of economic, technical, and sociological studies of individual applications of radioisotopes.

Other legal and economic studies on the application of sealed radiation sources and the consequences of employing radioisotopes in various other industries are being made. A statistical report on the use of radioactive substances from 1953 to 1963 will be published soon.

COOPERATION WITH NON-COMMUNITY COUNTRIES

The Eurisotop Bureau maintains direct contacts with official organizations in certain non-Community countries, as well as intra-Community relations with the major research establishments using isotopes. The following are examples:

The showing of a film in Moscow, Geneva, Vienna, and Iran on the use of radioisotopes.

The participation of a Swiss and an Israeli expert in the campaign to further the use of radioisotopes in the textile industry. The Bureau is in contact with the British textile industry and is negotiating a contract with the Argentine Atomic Energy Commission.

The attendance of a delegate from the British gas industry at a demonstration on the measurement of gas-duct leakages.

The cooperation of American, British, Israeli, and Austrian laboratories on a research contract in activation analysis.

The invitation by the Bureau to many activation analysis laboratories in non-Community countries to collaborate in its permanent information service.

The participation of Bureau Eurisotop in conferences and working parties within the International Atomic Energy Agency (IAEA) and the European Nuclear Energy Agency (ENEA).

PUBLICATIONS

Bureau Eurisotop is publishing a series of information booklets that are a valuable ad-

dition to the literature on the industrial and technical use of isotopes. The following have already been published or will be in the near future (the number is the Bureau Eurisotop Information Booklet number):

No. 1. *Bureau Eurisotop* (in French, German, Dutch, Italian), 1963. General information on the operation of Bureau Eurisotop.

No. 2. *Statistics on the Production and Use of Radioisotopes in the European Atomic Energy Community* (to be published soon).

No. 3. *Radioisotopes and Radiation in Industry and Technology: Economic and Technical Aspects* (in French, German, Dutch, Italian), June 1965. Information Booklet of Eurisotop, Series: Monograph-1. These papers were also published (in French) in *Belgicatom Assoc. Belge Develop. Pacifique Energie At. Bull. Inform.*, 8(45-46): (October 1963), after presentation at a series of meetings in Brussels, Mar. 12–29, 1963, sponsored by the Bank of Brussels and Bureau Eurisotop.

This booklet summarizes methods for the production of isotopes and discusses the uses of isotopes in the following industries: electronics, iron and steel, chemicals, pharmaceutical, textile, food, and machine building. Sections are also included on activation analysis and uses in internal medicine, hydrology, and agriculture.

No. 4. H. Wieczorek and H. Erhardt, *Technical-Economic Study of Two Cases of Level-Control by Radioisotopes in a Power Station* (in German), August 1965; (also in EUR-1909.d). Information Booklet of Eurisotop, Series: Case Study-1.

No. 5. *Activation Analysis, Comparative Bibliography* (in French, German, and Dutch), February 1965. Information Booklet of Bureau Eurisotop, Series: Bibliography-1. A compilation of 500 references on uses of activation analysis in industry. The bibliography is available on 3 by 5 cards and also as EUR-1886.f.

No. 6. O. Van Wauwe and D. Brandenburg, *Isotope Techniques and the Textile Industry—Literature Index* (in German), July 1965. Information Booklet of Eurisotop, Series: Bibliography-2. Contains about 115 references with broad subject, key-word, author, and corporate-author indexes.

No. 7. *Tracer Methods to Measure the Movement of Solids in Water*, Vol. 1. Brief Edition of the Reports and Discussions (in German), May 1965. Information Booklet of Eurisotop, Series: Proceedings-1. A summary of the discussions at a work session of Bureau Eurisotop held in Brussels Oct. 2–4, 1963. (For full papers see number 8 below.)

No. 8. *Tracer Methods to Measure the Movement of Solids in Water*, Vol. 2. Original Reports to the Work Session (in German), September 1965. Information Booklet of Eurisotop, Series: Proceedings-2. The full papers given at the work session of Bureau Eurisotop held in Brussels Oct. 2–4, 1963. The following papers were given:

The Problem of the Schelde River as an Access Way to Antwerp Harbor, by A. Sterling

The Origin of Ridges and Furrows in Riverflow Models, by J. Chabert and J. L. Chauvin

Technique Problems in Sand-migration Measurements with Radioactive Isotopes in Inner and Outer Jade Bay, by H. Fahse

Experimental Investigation of Solids Transport in Pressurized Streams, by I. Melisenda

Measurement of Solids Diffusion in Streams with Luminescence Indicators, by J. Chabert

Method of Using Fluorescence Indicators in Investigations on the Evolution of the Belgian Coast, by A. Bastin

Report on Experience in the Use of Radioactive Methods Within the European Community, by M. Petersen

Results of Sand-migration Investigations with Radioactive Isotopes in German Coastal Regions of the North and Baltic Sea, by H. Schulz

Measurement of Silt Drift with Radioactive Scandium Glass, by H. A. Klein

The Use of Radioactive Indicators for Investigating Solids Transport by Pushing Motions in Stung-Sen-Fluss in Cambodia, by F. Anguenot, J.-P. Carbonnel, G. Courtois, R. Danion, H. Forsberg, and M. Heuzel

Importance of Selecting the Kind and Particle Size of Radioactive Indicators According to the Object of the Investigation, by W. Nesteroff

Methods of Labeling Natural Sand Samples with Radioactive Material, by H. Becker and H. Gotte

Use of ^{192}Ir in Investigating Sediment Movement and Description of the Method of Surface Labeling of Sand Grains with ^{192}Ir, by G. Courtois and Ch. Rispal

Technique of Radioactive Labeling for Sand-migration Experiments in German Coastal Waters, by G. Meyn

Sand-migration Measurements with Radioactive Indicators in the Netherlands, 1957–1962, by J. Pilon

Handling and Inspection of Labeled Substances, by M. Petersen

Technique Problems in Sand-migration Measurements in German Coastal Waters, by G. Meyn

Development of Electronic Measuring Apparatus for Lifting-screws, by W. Petersen

Methods for Measuring Radioactive Deposition on the Spot, by J. Guizerix and G. Grandclement

Possibilities of Using a Limited Number of Radioactive Grains for Quantitative Investigations of Sediment Movement, by G. Courtois

The Use of Measurements of Natural Radiation Levels to Produce a Lithological Map of the Sea Bottom, by A. Bastin

Determination of the Residence Time of Activated Sludge in Purification Plants, by R. Krone

Measurement of Solids Throughput by Pushing Motions in Water Courses with Radioactive Indicators, by J. L. Chauvin and J. Danion

Penetration of a Water Course into the Ocean or a Lake, by J. Guizerix and G. Grandclement

Quantitative Understanding Sand Movement, by G. Schulze-Pillot

Results of an Inquiry of the French Atomic Energy Commission on the Economic Importance of Radioactive Material, by G. Robin

Risks and Necessary Protective Measures in the Use of Isotopes, by M. Petersen

Radioactive Labeling of Sludge – First Results of Surface Marking with ^{198}Au by the Method of M. Petersen, by G. Antier, A. Caillot, G. Courtois, and B. Jeanneau

Suggested Special Regulations in the Use of Artificial Radioisotopes for Investigating the Movement of Sediments, by G. Courtois and R. Hours

No. 9. *The Use of Radioisotopes in the Textile Industry.* (In preparation).

No. 10. H. Wieczorek and H. Erhardt, *Technical-Economic Study of Level Control through Radioisotopes in Rock Wool Production* (in German), September 1965. Information Booklet of Eurisotop, Series: Case Study-2. (Also in EUR-1909.d.)

No. 13. H. Wieczorek and H. Erhardt, *Technical-Economic Study of Level Measurement by Radioisotopes in Thermal Cracking* (in German), October 1965. Information Booklet of Eurisotop, Series: Case Study-3. (Also in EUR-1909.d.)

No. 14. H. Wieczorek and H. Erhardt, *Technical-Economic Study of Automatic Prevention of Mandrel Failure with Radioisotopes in Connection with the Pilger Cold Rolling Mill for Seamless Tubes* (in German), October 1965. Information Booklet of Eurisotop, Series: Case Study-4.) (Also in EUR-1909.d.)

Free copies of the above publications and further information about Bureau Eurisotop may be obtained from: Bureau Eurisotop, Euratom, 51-53 Rue Belliard, Brussels, Belgium.

Labeled Compounds

Euratom has included in its second five-year program[4] a threefold project in the field of labeled compounds which supplements and extends the program started in the first five-year program. The three objectives of the Euratom plan are to (1) build up a collection of labeled compounds that are not commercially available; (2) promote research on new methods for synthesis, purification, and storage of labeled compounds; and (3) promote the widest possible exchange of information on labeled compounds.

COLLECTION OF LABELED COMPOUNDS

Euratom has started a registry of needed and available labeled compounds. They hope in this way to bring together users who need a specific labeled material and producers who have more than enough of a material for their own needs.

The first list of available compounds was published as a report,[5] but more recently a list has been published monthly. The lists may be obtained from: Euratom, Directorate-General for Research and Training, "Labeled Compounds," 51-53 Rue Belliard, Brussels, Belgium. These notes on labeled compounds have as objectives (1) providing information on molecules that are not produced on a commercial scale, (2) gathering data on noncommercial compounds required, and (3) disseminating information on methods of synthesizing labeled molecules and on related problems. This labeled-molecule bank has already made it possible for many research laboratories to obtain compounds that were not otherwise available. It has also given industrial organizations the chance to market needed compounds without unduly expensive research.

RESEARCH ON LABELED COMPOUNDS

In Euratom contracts for the preparation of labeled molecules, the emphasis is placed on general methods rather than on the synthesis of specific compounds. The aim is to develop a production potential rather than to widen the range of compounds available. The Community has awarded more than a dozen contracts, which have led to the development of over 60 new labeled molecules. For example, compounds tagged with iodine, carbon, and tritium have been prepared for use in cancer, metabolism, and endocrine research, and 20 stable-isotope-labeled compounds have been prepared for studies in molecular spectrochemistry.

EXCHANGE OF INFORMATION

The third and final part of Euratom's work in promoting production and use of labeled com-

pounds is an aggressive information-exchange program. Several conferences have been sponsored and publication of a new periodical, *Journal of Labelled Compounds*, was started in 1965.

Brussels Conference in 1963. In 1963 Euratom sponsored a conference on labeled molecules in which 163 persons participated. The proceedings[6] contain papers and discussions in the four Euratom languages as well as English. All the non-English material is translated into English in a separate section of the book. The isotopes mentioned are ^{14}C, ^{32}P, ^{3}H, ^{131}I, ^{17}O, and ^{18}O. The compounds considered run the gamut of organic and biochemicals: olefins, alkaloids, chloramphenicols, aliphatic ketones, thyroxine, cholesterol derivatives, fatty acids, sugars, hydrocarbons, DNA and RNA, actinomycins, proteins, peptides, carboxylic acids, amino acids, curarizing compounds, hemoglobin, gibberellic acid, salicylic acid, steroids, and phenobarbital. Specific and general methods of preparation are discussed as well as storage problems.

Venice Symposium in 1964. The scope of the 1964 symposium in Venice was narrower than that of the 1963 meeting, being limited to biomedical material; the proceedings[7] are entirely in English. The isotopes mentioned include ^{3}H, ^{14}C, ^{131}I, ^{125}I, ^{36}Cl, ^{82}Br, and ^{18}F. A state-of-the-art review of recoil labeling is presented, together with a review of boron slow-neutron-capture therapy.

Other Conferences. A symposium on the use of tritiated nucleosides in metabolic studies was held in Mol in 1965, and one on labeled proteins and hormones in tracer studies was convened in Pisa in January 1966. A Second International Conference on Methods of Preparing and Storing Labeled Compounds is to be held in Brussels Nov. 28 – Dec. 3, 1966.

Journal of Labelled Compounds. This journal, which started publication in January 1965, has the stated objective:

> To publish papers on the preparation of new or existing compounds labelled with radioactive or stable isotopes, the improvement and generalisation of already-known methods, all problems directly concerned with preparation, purification, and analysis, and research in self-radiolysis and improvement of storage.

It is published quarterly by Euratom in Brussels, with papers in English, French, or German, and has an international editorial board.

The last section of this journal is a series of abstracts of articles on the synthesis and handling of labeled compounds. These abstracts, which are taken from 40 primary periodicals as well as *Nuclear Science Abstracts* and *Chemical Abstracts*, emphasize the aspects of the articles that are concerned with labeled compounds. This section is a continuation of a project started prior to the publication of the journal. Abstracts of articles appearing between May and December 1964 were given in a Euratom report[8] and supplement.[9]

(Robert H. Lafferty, Jr.)

Radioisotopes in Yugoslavia

The current status of radioisotope production and use in Yugoslavia is reviewed here. Yugoslavia's provisions for radioisotope production include the 6.5-Mw reactor at the Boris Kidrič Institute of Nuclear Sciences at Vinča, near Belgrade, the cyclotron at the Rudjer Bošković Nuclear Institute in Zagreb (deuterons up to 16 Mev), and a 200-kw TRIGA reactor planned for the Jožef Stefan Nuclear Institute in Ljubljana.[10] Procedures for production of radioisotopes and labeled compounds have been developed, and laboratories have been erected and equipment installed for both production of radioisotopes and labeled compounds and analytical work.

The Boris Kidrič Nuclear Institute started production of radioisotopes in 1961 and of labeled compounds in 1964. The Rudjer Bošković Nuclear Institute synthesized labeled compounds as early as 1957 and started production of radioisotopes in 1962. The Jožef Stefan Nuclear Institute has thus far worked solely on synthesis of labeled compounds.

Reactor Production of Radioisotopes; Labeled Compounds[11]

The 1964 production of radioisotopes in the Boris Kidrič research reactor was about three times that in 1961 (Table VII-1). The reactor, built in 1957, is fueled with uranium enriched to 2% and moderated with heavy water. Its 45 vertical channels are used for isotope production. The maximum thermal-neutron flux ranges from 6.5×10^{9} n/(cm^2)(sec) in channels used for biological investigations to

Table VII-1 PRODUCTION OF RADIOISOTOPES AT THE BORIS KIDRIČ INSTITUTE

Isotope	Production, mc			
	1961	1962	1963	1964 (up to Sept. 1)
^{198}Au	26	4,417		4,399
^{131}I	332	6,671	3,766	8,726
^{32}P	168	532	440	1,029
^{35}S	11	29	257	104
^{42}K		72		
^{24}Na		24		
^{131}Ba		2,888		
^{82}Br		1,940		
^{41}Ar		24,000		
^{51}Cr				4,000
^{45}Ca, ^{65}Zn, ^{60}Co, ^{89}Sr, ^{59}Fe, ^{141}Ce (solutions)			0.5	83
^{204}Tl		2		
^{192}Ir	142,000	263,240	303,100	393,550
^{60}Co	8,932	231,205	16,757	12,199
Irradiated material	66,978	108,795	78,726	81,611
	218,447	643,815	403,046	505,701

5.13×10^{13} n/(cm^2)(sec) in the central channel.[12–15] Vacuum facilities and a laboratory are nearby for investigations with short-lived isotopes.

While the reactor was being installed, design and construction were proceeding on a building to house the Hot Laboratory, the largest part of whose space (667 m^2) is for production of high-activity radioisotopes.[16] There are two laboratories for synthesis of labeled compounds, one for analysis, and rooms for activity measurements, physicochemical measurements, and chromatography.

Irradiated targets are chemically processed in the Hot Laboratory to separate the desired products. Some of the methods used are based on the results of earlier physicochemical studies[17–24] of sorption on Al_2O_3, silica gel, MgO, and Mg; other methods are entirely original. The isotopes produced include ^{42}K, ^{24}Na, ^{45}Ca, and ^{89}Sr from irradiated carbonates; ^{60}Co, ^{65}Zn, and ^{110}Ag from irradiated metals; and ^{32}P with carrier (Refs. 25, 26), ^{141}Ce, and ^{59}Fe from irradiated oxides.

The more important procedures currently in use for producing carrier-free isotopes are:

Sulfur-35: Irradiated KCl is dissolved in dilute HCl, and the ^{35}S, ^{32}P, and ^{36}Cl are adsorbed on Al_2O_3 and selectively eluted.[27,28]

Phosphorus-32: Irradiated $MgSO_4$ is dissolved in water, and the ^{32}P is adsorbed on MgO and then on Dowex 50.[29]

Iodine-131: Irradiated dehydrated telluric acid is dissolved in 10% KOH, and the ^{131}I is distilled from the treated solution.[30,31]

Gold-198: Irradiated 99.999% pure gold metal is dissolved in aqua regia, and the gold is recovered from the treated solution. In some cases it is converted to colloidal form.[32]

Chromium-51: Irradiated K_2CrO_4 is dissolved in water, and the chromium is adsorbed on sintered glass and recovered as sodium chromate.[33]

Radiation sources are made[34–38] for radiography (^{192}Ir, ^{60}Co) and radiochemical work as well as radioisotopes for medical use. Chemical and radiochemical purity and sterility control are especially important in the production of pharmaceuticals.[39–44]

Since 1962, work has been intensified on synthesis of labeled compounds to make possible the synthesis of compounds needed for research by both the Institute itself and other institutions. Compounds first were synthesized with ^{14}C, and later with ^{35}S and ^{32}P; synthesis of compounds labeled with ^{3}H and halogens is now planned. Procedures[45–55] have been developed for production of 18 compounds labeled with ^{14}C, 6 with ^{35}S, and 5 with ^{32}P.

The Institute issued a catalog of radioactive products[56] in 1963, which includes information on conditions under which they supply radioactive products and render other services. They have 87 regular domestic customers, including 40 industrial, 24 medical, and 19 scientific groups. In 1964 the Institute delivered its first shipments abroad and in 1965 supplied the first 1000-curie ^{60}Co source, for a teletherapy unit, to the Elektroindustrija (El) firm in Niš.

Cyclotron Production of Radioisotopes; Labeled Compounds[57,58]

Radioisotopes regularly produced in the Rudjer Bošković cyclotron include ^{22}Na, ^{24}Na, ^{56}Co, ^{57}Co, ^{58}Co, ^{65}Zn, and ^{120}Sb, some with high specific activity and carrier free (Table VII-2). Nuclear reactions that occur during their production in the 15-Mev deuteron beam are (d,α), (d,n), and $(d,2n)$ with light, medium, and heavy nuclei, respectively. The (d,p) reaction is seldom used because products obtained by it are identical to (n,γ) products obtained with the reactor thermal-neutron beam.

In order to satisfy increasing demands, a new program for cyclotron production of radionuclides is being launched. Medical, physical, and biological institutions have become regular customers, and production of ^{54}Mn, ^{55}Fe, ^{74}As, ^{181}W, and ^{206}Bi in the internal cyclotron beam by deuteron reactions is being considered. Construction of an ion source that would pro-

Table VII-2 HIGH-SPECIFIC-ACTIVITY AND CARRIER-FREE RADIOISOTOPES PRODUCED AT RUDJER BOŠKOVIĆ INSTITUTE

Radionuclide	Reaction	Half-life	Decay	Specific activity of product	Parallel nuclear reactions
^{22}Na	$^{24}Mg(d,\alpha)^{22}Na$	2.6 years	89% β^+ 11% EC	Carrier free	$^{26}Mg(d,\alpha)^{24}Na$
^{24}Na	$^{26}Mg(d,\alpha)^{24}Na$	15 hr	100% β^-	Very high	$^{24}Mg(d,\alpha)^{22}Na$
^{57}Co	$^{56}Fe(d,n)^{57}Co$ $^{57}Fe(d,2n)^{57}Co$	267 days	100% EC	Carrier free	$^{58}Fe(d,2n)^{58}Co$ $^{57}Fe(d,n)^{58}Co$ $^{58}Fe(d,2n)^{58}Co$
^{65}Zn	$^{65}Cu(d,2n)^{65}Zn$	245 days	98.5% EC 1.5% β^+	Carrier free	$^{63}Cu(d,2n)^{63}Zn$
^{120}Sb	$^{120}Sn(d,2n)^{120}Sb$ $^{119}Sn(d,n)^{120}Sb$	5.8 days	100% EC	Very high	$^{122}Sn(d,2n)^{122}Sb$ $^{124}Sn(d,2n)^{124}Sb$

duce 32-Mev α particles is also planned, with ^{83}Rb to be the first radionuclide produced. The external cyclotron beam is also to be used. Setting the target behind the deflector could make possible the irradiation of powders, e.g., oxides, salts, and low-melting-point metals, and ^{51}Cr, ^{71}Ge, ^{75}Se, ^{83}Rb, ^{103}Pd, ^{133}Ba, and ^{139}Ce are to be produced in this arrangement.

Another internal neutron target is to be installed later for producing fast neutrons. Well-known nuclear reactions on light nuclei will be used, and ^{22}Na will be produced from a magnesium target.

The Radioisotope Laboratory was set up in 1954 for (1) synthesizing ^{14}C-labeled compounds for its own research and for that of other laboratories in the country; and (2) studying, by the ^{14}C tracer technique, the metabolism of biologically interesting compounds, particularly the biogenic amines and amino acids. Most of the labeled compounds synthesized had not been previously prepared with radioactive tracers, and, after a series of experiments with inactive materials, the procedures for synthesis with tracers were worked out.

Starting with one-carbon molecules labeled with ^{14}C, the staff has synthesized a number of labeled compounds:

From methyl-^{14}C iodide: L- and D-α- and L- and D-β-methionine-methyl-^{14}C have been obtained. Also, D,L -^{14}C-sphingin (1-hydroxyl-2-aminooctadecane-1-^{14}C) was synthesized for the Radiological Laboratory.

From $Ba^{14}CO_3$: N-acetyl-D,L-serine-β-^{14}C was synthesized and then enzymatically split for use in studying methylation in plants and animals. Likewise, α-naphthylisocyanate-^{14}C was synthesized for investigations of the mechanism of the ureido ester → diacylated amine reaction, and from this isocyanate derivative the ethyl esters of α- and β-naphthylureido-(^{14}C-carbonyl) propionic acid were prepared. Novocaine (2-diethylaminoethyl ester of β-aminobenzoic acid) labeled with ^{14}C in the carboxyl group was produced for the Medical College in Ljubljana. Work is nearing completion on the synthesis of labeled hexachlorophene [2,2-methylene-^{14}C-bis(3,4,6-trichlorophenol)] for the Radioisotope Laboratory of the Veterinary College in Zagreb.

From $Na^{14}CN$: The biogenic amine serotonin labeled on the 1'-C atom of the side chain has been synthesized for use in both in vivo and in vitro experiments on the metabolism and function of this amine. So far attempts to prepare serotonin labeled in the indole ring have been unsuccessful, but a simple method has been worked out for preparing 3,5-disubstituted indoles. A procedure has been developed for synthesis of the labeled herbicide Symazin [2-chloro-4,6-bis(ethylamine)-α-triazine] for the Institute for the Application of Nuclear Energy in Agriculture, Veterinary Sciences, and Forestry, at Zemun, near Belgrade.

During synthesis of these compounds, it has often been necessary to prepare as intermediate products some substances of interest for the investigation of other problems. Some of the more important ones are formaldehyde-^{14}C, diazomethane-^{14}C, benzoic acid-carboxyl-^{14}C, *N*-methylphthalimide-methyl-^{14}C, acetonitrile-1-^{14}C, ethylamine-1-^{14}C, *p*-aminobenzoic acid-carboxyl-^{14}C, α-naphthoic acid-carboxyl-^{14}C, 5-benzyloxyindolyl-3-acetonitrile-1'-^{14}C, 5-benzyloxyindolyl-3-octene acid-carboxyl-^{14}C, and 5-hydroxyindolyl-3-octene acid-carboxyl-^{14}C.

Use of Radioisotopes in Veterinary Medicine[59]

As a branch of applied biology, veterinary medicine work is concerned with improvements in livestock production and protection of animal health, and radioisotopes are being used in both scientific research and in processing of animal products.

The use of radioisotopes in veterinary research in Yugoslavia dates as far back as 1952,

when M. Jovanović used ^{32}P for studying the effect of vitamin D on the loss of phosphorus from the isolated heart. Today there are centers for application of nuclear energy in agriculture, veterinary medicine, and forestry in Belgrade and Zagreb; fundamental problems are being studied in the biological departments of the nuclear institutes; and radioisotope techniques are being used in research at the Veterinary Colleges in Sarajevo and Ljubljana. Such developments are being considerably advanced by the United Nations Special Fund Project, "Nuclear Research and Training in Agriculture." Its main objectives are the extension of nuclear research and the training of staff in agriculture and animal breeding.

In the years of organized work on the application of nuclear energy in agriculture and farming, results have been good. Some of the results are already being used in practice. In addition to antihelminthic vaccine, procedures using radioisotopes have been introduced in the diagnosis of disease and therapy of farm animals. Methods have been developed for determining the degree of contamination of foods (eggs), and a criterion has been developed for assessment of their usability. Increased and broader use of scientific results achieved in everyday practice and work on current problems of livestock production are undoubtedly the most important future tasks.

Third Symposium on Use of Radioisotopes and Radiation in Industry[60]

The third Yugoslavian symposium on industrial use of radioisotopes and radiation was held in Herceg Novi on May 10–14, 1965. Sponsored by the Federal Nuclear Energy Commission and the Federal Economic Board of Belgrade, its purposes were to stimulate the use of radioisotopes in industry, hydrology, and other fields and to solve some of the problems of production of radioisotopes, compounds, and instruments needed for the application of radioisotopes and radiation.

Some 40 papers were presented on the production of radioisotopes, sources, and labeled compounds and on the use of radioactive tracers, of level, thickness, and moisture gages, and of radiography. The fields covered were foods, machinery, hydrology, hydroelectric plants, metallurgy, and prospecting. Prospects for radiochemical processing and polymerization were discussed.

Cobalt-60 Radiation Unit

There is a new 2-kc ^{60}Co radiation unit at Boris Kidrič Institute. Its possible uses include chemical synthesis, polymerization, vulcanization of rubber, food preservation, and sterilization of drugs and medical equipment.[61]

(Martha Gerrard)

Radioisotopes in Australia

The current status of and recent developments in radioisotope use and production in Australia are reviewed here and illustrated with a few specific examples. The Australian Atomic Energy Commission (AAEC), through its Isotopes Division, conducts research on both applications and production of radioisotopes and sources. Although savings resulting from the use of radioisotopes cannot be easily estimated, experience indicates that costs of the experimental work are small compared to the economies achieved. The AAEC encourages private consulting groups to provide service to industry in established radioisotope techniques and assists such groups by providing training and lending equipment during the formative stages.

The AAEC began producing radioisotopes in April 1960, and that same year sponsored a conference on uses of radiation.[62a] By 1964–1965 they were making more than 800 shipments annually[62b] with a total value of 32,383 pounds ($70,000). Of this value, 45% represents medical uses, 29% industrial uses, 23% nonmedical research uses, and 3% export. The 1965–1970 production program allows for an increasing supply of radiochemicals and radiopharmaceutical preparations, partly as a result of construction of a new radiochemical laboratory. Its capacity will be sufficient to supply all the short- and intermediate-half-life radioisotopes required in Australia.

The AAEC facilities[63] at Lucas Heights (near Sydney) for radioisotope production consist of the High Flux Australian Reactor (HIFAR), a 1.3-Mev Van de Graaff accelerator, an irradiation pond, and cells for handling high- and

medium-activity material. The HIFAR produces ^{60}Co with specific activity up to 250 curies/g for making sources for both domestic use and export.[64] Sources are currently made by irradiation of aluminum-encapsulated cobalt disks of 12 or 17 mm diameter and 1 to 2.5 mm thickness for up to 3 years. The disks are assembled, either still encapsulated or bare, in stainless-steel containers, which are sealed and mounted for the teletherapy head.

There is also a low-flux reactor, the MOATA, which is used for some activation studies. A pilot plant for studying process radiation contains 70 spent fuel elements, which are used to irradiate bulk material while they decay to a sufficiently low level to permit chemical processing. The capacity of the plant is equivalent to that of one using 200,000 curies of ^{60}Co, and the work there is demonstrating that spent fuel elements can provide a feasible industrial source of radiation.

Progress in AAEC projects is reported in technical journals, in Commission-sponsored topical reports, in annual reports, and in *Atomic Energy in Australia*, a quarterly publication started in 1957.

Use of Sources

LARGE SOURCES

Among the studies involving large sources is that of food preservation by irradiation. Some of the foodstuffs currently under investigation are potatoes,[65] beans,[66] and fruit. Preliminary designs have been made of a grain irradiator with 100 tons/hr capacity and of a mobile irradiator that could be used to demonstrate irradiation processing in agriculture and industry.[62]

The use of radiation to sterilize pharmaceuticals is increasing, and studies have been started[62] on doses and conditions needed to produce sterilized pyrogen-free aqueous parenteral solutions. A pyrogen-testing unit was developed, and it was shown that a radiation dose of 2.5 Mrads does not produce a pyrogenic reaction in physiological saline. The effect of radiation on various polyethylene formulations suitable for packaging of fluids is being studied.

The possibility of irradiation stabilization of lumber additives for prevention of shrinkage during drying is under consideration.[62]

Interest has been shown in the production of useful mutations in industrial crops by irradiation.[67]

The use of ^{60}Co sources[68] for cancer therapy[68d] and for sterilization of hides is well established. The plant[68c] operated by Gamma Sterilization Pty. Ltd. for industrial sterilization by ^{60}Co gamma irradiation is the largest in the world. Its primary purpose was disinfection of imported animal fibers used in carpet manufacture, but it is being used increasingly for sterilization of hospital supplies and pharmaceuticals. Built in 1959, it has a design capacity of 10,000 tons/year and is large enough to house, eventually, 2×10^6 curies of ^{60}Co.

SMALL SOURCES

The AAEC makes ^{192}Ir and ^{60}Co sources for gamma radiography and is developing ^{170}Tm and ^{134}Cs sources.[69] They supplied the ^{192}Ir sources used in the gamma radiography of welds at the New Zealand geothermal steam power station.[70] Work to improve the design and encapsulation methods for sealed radiography and gage sources of radioactive cobalt, iridium, thulium, and cesium will probably result in substitution of titanium for aluminum as canning material and use of electron-beam welding for sealing the capsules.[62,69] The use of radioisotope gages is well established in Australia, and the newly organized Non-Destructive Testing Association of Australia includes the use of radioisotopes for industrial radiography and quality control in its scope.[71]

The slope and extent of cracks in a mine roof are routinely determined by inserting a ^{192}Ir or ^{137}Cs gamma-emitting strip source in a borehole and determining the variation in radiation 40 to 60 cm away as the source and detector are moved.[63]

Gamma-Excited X-Ray Sources. Gamma-excited X-ray sources have been studied at Lucas Heights, and work is continuing on expanding their applications.[72] Their monoenergetic X-ray output, low cost, and ruggedness make them particularly suitable for industrial applications. A promising application under investigation is the measurement of tin-plate thickness and of the silver content of photographic emulsions.[73]

Neutron Sources. Semiportable neutron sources with outputs of about 10^5 n/sec have been made from $^{124}Sb-Be$ and $^{24}Na-D_2O$, with

gamma activities of 105 and 52 mc, respectively. A source was developed with a detachable guide rod for transferring the gamma emitter when a collimated beam is required.[63]

Implants. Gold-198, ^{182}Ta, ^{60}Co, and ^{90}Y implants are made and used in medicine.

Use of Tracers

INDUSTRY

Mixing. The efficiency of a 20,000-gal raw-sugar subsider was determined[74] by observing the path of ^{82}Br (5 mc per pound of KBr in solution). In another sugar-plant test, circulation patterns in vacuum pans were found with 100 mc of $^{24}Na_2CO_3$, contained in a rubber ball whose density was adjusted to that of the solution.[63] The holdup time in a spiral mixer where a few ounces of a powdered solid was blended with hundreds of pounds of another was cut from 20 min to 3 min after tests with 1 mc of ^{131}I-labeled potassium iodide showed that mixing was accomplished in the shorter time.[74] Scintillation detectors placed at each end of the mixer showed that mixing was complete in 3 min (Fig. VII-1).

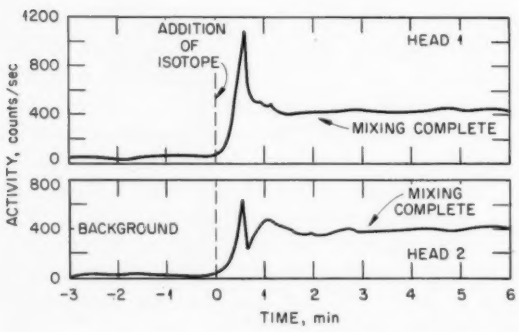


Fig. VII-1 Recorder traces in mixing experiment.

Leak Detection. Oil leaks in an air-separation plant have been determined with oils labeled separately with ^{198}Au and ^{131}I to identify the origin of the contamination. In a novel project, the point of ingress of carbon monoxide to an airplane cabin during flight was found[62,85] by use of radioactive krypton. Special technicians were not required; the equipment was used by the usual crew after training.

A rapid method for detecting leaks in public-service gas pipes with $CH_3{}^{82}Br$ was developed.[75]

Process Flow. The gamma emitter ^{198}Au was used to measure the flow rate of water in an air-conditioning unit.[76]

Development of Tracers. Because of their short lives, ^{198}Au (2.7 days) and ^{24}Na (15.4 hr) are important industrial tracers. In studies on organic-soluble forms, secondary amines were found[77] useful for complexing gold. Sodium-24 has been used to form an oil-soluble salt of a mixture of highly branched C_9 to C_{11} carboxylic acids,[63] which is preferable to the naphthenate.

HYDROLOGY

The movement of water under various conditions is studied with radioisotopes.[62,63,75] The flow rate in streams has been determined with ^{198}Au and ^{82}Br by both the total-count method of Hull[78] and the continuous-sampling method. The flow of water into a power-station cooling pond was determined with ^{131}I, and the paths of liquid effluents from a sewage-treatment plant and from a proposed industrial plant were studied with ^{198}Au. To obtain information on an aquifer, both ^{131}I and ^{3}H were injected[79] into a borehole at the level of the aquifer and traced for some 20 m.

Radioisotopes are also widely used to study the deposition of solids suspended in water (Refs. 62, 63, 74, 75, and 80). The effect of tide on movement of silt was determined by observing, with an underwater detector, silt labeled with ^{64}Cu (15 curies per 60 lb of silt) and deposited on a harbor floor in New South Wales. The isotopes $^{140}Ba-^{140}La$ (100 mc/100 g) and ^{198}Au (10 curies/15 lb) were used in other tests. Before locating a new thermal-power station, the feasibility of disposing of the fly ash in the ocean was investigated with ^{198}Au-labeled ash. Data obtained with radioisotopes in two large-scale experiments in Botany Bay will be used in assessing the feasibility of developing a deep-water port. The first experiment was short and used sand labeled[81] by being silver plated and then exposed to ^{198}Au solution. The second experiment, a long-term one, is using 600 lb of sand labeled with about 300 curies of ^{51}Cr.

Computer programs have been developed[62] to process the results of large-scale hydrological experiments using radioisotopes. The results are shown as contour maps from which the movement of the labeled material can be readily determined.

MEDICINE

Medical radioisotopes now available from the AAEC are ^{24}Na, ^{42}K, ^{82}Br, and ^{32}P, some as sterile solutions. Products expected to be available shortly are ^{131}I, ^{197}Hg-labeled Neohydrin, ^{99m}Tc, ^{64}Cu-EDTA, ^{18}F, ^{131}Cs, and various radiocolloids.

Radioisotopes being used in dental research at the University of Sydney include ^{32}P, ^{45}Ca, ^{18}F, and ^{131}I for studying such physiological processes as placental transfer of elements in rats.[82] The aim of this study is to help the dentist understand the way in which dietary fluoride is utilized by mother and fetus.

METEOROLOGY

In a technique developed to trace air movements in clouds, fine particles of ^{64}CuO are released from an aircraft and followed with a scintillometer.[83] In large-scale ventilation and air-pollution studies, the ^{64}CuO particles that are released are collected on filter paper with a high-speed air sampler.[75]

RESEARCH

Physical properties of sulfur have been studied[84] with ^{35}S. (Martha Gerrard)

Importation of Radioisotopes into West Germany

A recent article in *Atomwirtschaft** gives statistics on the radioisotope imports into West Germany. Excluding radioisotope irradiation sources of over 50 curies, the total curies imported were approximately 20 thousand for 1964, 11 thousand for 1963, but only 17 thousand for the entire period 1956–1962. Twenty-two different nuclides in quantities above 1 curie were included, but ^{192}Ir, ^{60}Co, ^{90}Sr, and ^{3}H constituted over 90% of the imports. Iridium-192 was used primarily for materials testing and cancer therapy, ^{60}Co for gaging and other purposes, ^{90}Sr for studying the conversion of isotopic heat into electrical energy, and ^{3}H and ^{147}Pm for luminous paints and pigments.

Imports of radiation sources greater than 50 curies appear to have leveled off, at least for the present, at somewhat under 50 thousand curies per year. On a curie basis, about 15 to 20 times as much ^{60}Co is imported each year as the next most imported source material, ^{137}Cs. Preservation of foods and sterilization of medical supplies by radiation are still prohibited by law in West Germany; however, when these are permitted, an increase will be expected in the use of larger sources. Of the 27 large sources imported in 1964, 18 were for radiation therapy and the remainder for radiation chemistry and other uses.

Over one-half of all the radioactive material imported was supplied by Canada; Great Britain and the United States were the next largest suppliers with 13 and 10%, respectively. The remainder was supplied from several other countries. (R. E. Greene)

Availability of Stable Isotopes in East Germany

The German Association for Basic Industry in Leipzig issued a catalog of stable isotopes in 1964. Printed in both Russian and German, the catalog was compiled to publicize the variety of enriched stable isotopes, labeled substances, and targets available in the USSR and East Germany.

Comparison of the availabilities of East German items with those from Oak Ridge National Laboratory and other U. S. suppliers is of interest because of the differences in some of the enrichment values. For example, the German enrichments are higher in some cases than the U. S. (see Table VII-3).

More often, however, the U. S. enrichments are higher (Table VII-4).

The isotopes of mercury (except for ^{198}Hg from gold), chlorine, bromine, krypton, and xenon are not listed in the catalog as having been separated, but most of these isotopes are available from the United States in the enrichments shown in Table VII-5.

Also of interest is the variety of targets that are available; see Table VII-6, which is reproduced (and translated) from the catalog.

Data related to isotope targets that are prepared directly in the electromagnetic separators are given in Table VII-7. (P. S. Baker)

*Statistical Data on German Imports of Radioactive Substances, *Atomwirtschaft*, 10(6): 303 (1965), in German. (ORNL-tr-1032 by Martha Gerrard)

Table VII-3

Nuclide	Enrichment, % East German	Enrichment, % U. S.	Nuclide	Enrichment, % East German	Enrichment, % U. S.
^{102}Pd	Not separated	65	^{108}Pd	98	95
^{104}Pd	88	85	^{110}Pd	98	95
^{105}Pd	95	80	^{162}Er	26	20
^{106}Pd	98	85	^{164}Er	76	63

Table VII-4

Nuclide	Enrichment, % East German	Enrichment, % U. S.	Nuclide	Enrichment, % East German	Enrichment, % U. S.
^{18}O	4–10	97	^{82}Se	74	90
^{29}Si	69	95	^{87}Sr	74	98
^{30}Si	66	95.5	^{96}Zr	58	90
^{40}K	2.8	80	^{102}Pd	39	65
^{42}Ca	69	> 85	^{108}Cd	60	75
^{43}Ca	40	> 65	^{111}Cd	80	95
^{44}Ca	94	> 98	^{116}Cd	84	95
^{46}Ca	4.8	30	^{115}In	81	98
^{48}Ca	67	> 95	^{119}Sn	75	90
^{46}Ti	74	90	^{122}Sn	83	95
^{47}Ti	76	90	^{120}Te	33	53
^{48}Ti	98	> 97	^{130}Ba	23	> 50
^{49}Ti	71	90	^{132}Ba	12	45
^{50}Ti	57	85	^{134}Ba	76	85
^{50}V	28	45	^{138}La	1.0	1.9
^{50}Cr	88	> 95	^{156}Dy	3.0	25
^{54}Cr	80	> 95	^{158}Dy	10.0	25
^{57}Fe	79	> 93	^{160}Dy	50	70
^{58}Fe	52	85	^{176}Lu	35	80
^{61}Ni	80	95	^{174}Hf	10	20
^{64}Ni	80	99	^{185}Re	81	99
^{67}Zn	71	95	^{191}Ir	84	96
^{70}Zn	45	> 75	^{190}Pt		0.9
^{73}Ge	79	95	^{204}Pb	58	> 99
^{74}Se	41	59	^{206}Pb	97	> 99.95

Table VII-5

Nuclide	Enrichment, %	Nuclide	Enrichment, %
^{35}Cl	> 98	^{129}Xe	60
^{37}Cl	> 98	^{130}Xe	80
^{85}Br	> 98	^{196}Hg	64
^{87}Br	> 98	^{198}Hg	> 99
^{78}Kr	8	^{199}Hg	90
^{80}Kr	23	^{200}Hg	90
^{86}Kr	> 99	^{201}Hg	90
^{124}Xe	> 2	^{202}Hg	99
^{126}Xe	1	^{204}Hg	> 80
^{128}Xe	8		

Table VII-6

Element	Isotope	Method of preparation*	Target thickness, μ
Mg	24, 25, 26	ev.	2–10
Ti	46, 47, 48, 49, 50	th.	1–10
Cr	50, 52, 53, 54	e.d.	0.7
		th.	1–10
Fe	54, 56, 57, 58	e.d.	0.6
Ni	58, 60, 61, 62, 64	e.d.	0.2
Zn	64, 66, 67, 68, 70	e.d.	1.5
Ca	63, 65	e.d.	1.5–10
Zr	90, 91, 92, 94, 96	th.	1–10
Ag	107, 109	e.d.	2–10
Cd	106, 108, 110, 111, 112, 113, 114, 116	e.d.	6–9
Sn	112, 114, 115, 116, 117, 118, 119, 120, 122, 124	e.d.	1–5
Eu	151, 153	ev.	1–10
Gd	152, 154, 155, 156, 157, 158, 160	ev.	1–10
Pt	190, 192, 194, 195, 196, 198	e.d.	1–10
Pb	202, 204, 206, 207, 208	e.d.	5

Unsupported metal foils of the isotopes of Ga, In, Re, and Tl can also be fabricated.

*ev. = evaporation; th. = thermal cracking; e.d. = electrodeposition.

Table VII-7

Element	Isotope	Method of preparation*	Target thickness, $\mu g/cm^2$
Li	6, 7	d.b.	20
B	10, 11	d.b.	1000
C	12, 13	d.b.	10–20
N	14, 15	d.b.	10–20
O	16, 18	d.b.	10–20
F	19	d.b.	10–20
Ne	20, 21, 22	d.b.	1–3
Mg	24, 25, 26	d.b.	30–40
Al	27	d.b.	100
Si	28, 29, 30	d.b.	100
		s.	1000
S	32, 33, 34	d.b.	100
Cl	35, 37	d.b.	10–20
Ar	36, 40	d.b.	1–3
K	39, 41	d.b.	100
Ca	40, 42, 43, 44, 48	d.b.	100
		s.	5000
Ti	46, 47, 48, 49, 50	d.b.	100
Cr	50, 52, 53, 54	d.b.	20
Fe	54, 56, 57, 58	d.b.	20–30
Ni	58, 60, 61, 62, 64	d.b.	100
Cu	63, 65	d.b.	10
Zn	64, 66, 67, 68, 70	d.b.	10
Ge	70, 72, 73, 74, 76	d.b.	6
		s.	5000
Kr	80, 82, 83, 84, 86	d.b.	1–3
Sr	86, 87, 88	d.b.	30
		s.	1000
Zr	90, 91, 92, 94, 96	d.b.	30
		s.	1000
Ru	99, 100, 101, 102, 104	d.b.	50
		s.	200
Pd	104, 105, 106, 108, 110	d.b.	30
		s.	100
Cd	106, 108, 110, 111, 112, 113, 114, 116	s.	1000
Xe	129, 130, 131, 132, 134, 136	d.b.	1–3
Ba	134, 135, 136, 137, 138	d.b.	20–30
La	139	d.b.	20–30
Sm	144, 147, 148, 149, 150, 152, 154	d.b.	50
		s.	5000
Eu	151, 153	s.	5000
Gd	152, 154, 155, 156, 157, 158, 160	d.b.	50
		s.	5000
Dy	160, 161, 162, 163, 164	d.b.	50
		s.	5000
Er	166, 167, 168, 170	s.	5000
Yb	171, 172, 173, 174, 176	s.	5000
Lu	175, 176	s.	5000
Hf	178, 179, 180	s.	5000
W	182, 183, 184, 186	s.	1000
Ir	191, 193	d.b.	10
		s.	100

*d.b. = direct bombardment; s. = sputtering.

References

Radioisotope Programs in Euratom

1. Euratom 1965, Eighth General Report, March 1964–February 1965, Euratom Report, pp. 37-38, March 1965.
2. Euratom 1965, Documentation Attached to Eighth General Report, Document 12–Industrial Applications of Radioisotopes and Radiation, Euratom Report, pp. 69-72, March 1965.
3. G. Pröpstl, Radioisotopes and Radiation in the Textile Industry, *Euratom Bull.*, 4(1): 24-29 (March 1965).
4. Euratom 1965, Documentation Attached to Eighth General Report, Document 11–Labelled Molecules and Radioisotopes, Euratom Report, pp. 63-67, March 1965.
5. Collection of Marked Compounds, Euratom Report EUR-1801.e, 1964.
6. J. Sirchis (Ed.), Proceedings of the Conference on Methods of Preparing and Storing Marked

Molecules, Brussels, Nov. 13–16, 1963, Euratom Report EUR-1625.e, 1359 pp., 1964.
7. J. Sirchis (Ed.), Preparation and Bio-Medical Applications of Labeled Molecules, Symposium Proceedings, Venice, 1964, Euratom Report EUR-2200.e, 502 pp., December 1964.
8. H. Dworschak and J. Sirchis, Abstracts on Labeled Compounds, Euratom Report EUR-2212.e, 1964.
9. H. Dworschak and J. Sirchis, Abstracts on Labeled Compounds, Euratom Report EUR-2212.e (Suppl.), 1965.

Radioisotopes in Yugoslavia

The references marked with an asterisk were taken directly from Ref. 11*a* and were not examined by the reviewer.

10. V. Jezdić, Radioisotopes, *Nukl. Energ.*, 2(2): 1 (1965) (in Serbo-Croatian).
11. *a.* Č. Teofilovski and V. Jezdić, Production of Radioisotopes and Labeled Compounds at the Boris Kidrič Institute of Nuclear Sciences, *Nukl. Energ.*, 2(2): 2-9 (1965) (in Serbo-Croatian).
b. Yugoslavia: Radionuclide Production, *Atomwirtschaft*, 10: 488 (1965) (in German) (summary of Ref. 11*a*).
12.*Z. Dizdar, Production of Radioisotopes at the Boris Kidrič Institute, *Nova Proizvodnja*, 11: 228 (1960) (in Serbo-Croatian).
13. Č. Teofilovski, Production of Artificial Radioactive Isotopes, *Tehnika (Belgrade)*, 17: 837-842 (1962) (in Serbo-Croatian) (English translation JPRS-14524).
14. *a.* Č. Teofilovski and Z. Dizdar, Production of Radioactive Isotopes at the Boris Kidrič Institute in Vinča, *Tehnika (Belgrade)*, 19: 25-32 (1964) (in Serbo-Croatian) (English translation JPRS-23279).
b. R. Drašković, Radioactive Isotope Production Development at the Boris Kidrič Institute in Vinča, *Tehnika (Belgrade)*, 20: 650-652 (1965) (in Serbo-Croatian) (English translation JPRS-30769).
15. *a.* Z. Dizdar, Production of Radioisotopes on the RA Research Reactor in Yugoslavia, Study Group Meeting on Research Reactor Utilization, Athens, Sept. 9–13, 1963 (IAEA, Vol. II).
b. Č. Teofilovski, Yugoslav Radioactive Products for Industrial Uses, *Tehnika (Belgrade)*, 20: 644-649 (1965) (in Serbo-Croatian) (English translation JPRS-30771).
16. Z. Dizdar, Laboratory for High-Activity Chemistry at the Boris Kidrič Institute in Vinča, *Nukl. Energ.*, 1(1): 7-9 (1964) (in Serbo-Croatian).
17. O. Ž. Kovačević and S. Stanković, Preparation of Carrier-Free Radioactive ^{32}P, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 6: 159-161 (1956).
18. S. R. Veljković and S. M. Milenković, Concentration of Carrier-Free Radioisotopes by Adsorption on Alumina, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958*, Vol. 20, pp. 45-49, United Nations, New York, 1958.
19. S. Veljković and S. Milenković, Concentration of Carrier-Free ^{32}P by Adsorption on Alumina, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 10: 61-69 (1960).
20. S. R. Veljković, J. V. Stevović, and O. I. Mirić, Activated Exchange on Inorganic Crystals, *Chemical Effects of Nuclear Transformations*, Symposium Proceedings, Prague, 1960, Vol. 1, pp. 465-473, International Atomic Energy Agency, Vienna, 1961 (STI/PUB/34).
21. S. Milenković, Z. Dizdar, and J. L. Servian, Separation of ^{35}S, ^{32}P, and ^{36}Cl on Alumina, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 12: 81-88 (1961).
22. O. Ž. Jovanović-Kovačević, Separation of Carrier-Free ^{32}P from Elementary Sulfur on a Silica Gel Column, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 10: 51-59 (1960).
23. S. R. Veljković and S. M. Milenković, Separation of ^{32}P from ^{35}S and from Some Other Anions on MgO, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 10: 71-74 (1960).
24. O. Ž. Jovanović-Kovačević, S. Milenković, and Č. M. Teofilovski, Concentration of ^{32}P from Irradiated $MgSO_4$ by Adsorption on Metallic Magnesium, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 13(4): 1-8 (1962).
25. S. Milenković, Č. Teofilovski, Z. Dizdar, and Lj. Birčanin, A New Procedure for the Production of Carrier-free ^{35}S, *Bull. Inst. Sci. "Boris Kidrich,"* 12: 89-95 (1961).
26. O. Ž. Jovanovič-Kovačević and P. M. Janićijević, Some New Developments in the Production of Carrier-Free ^{32}P, *Atompraxis*, 10: 265-267 (1964).
27.*O. Ž. Jovanović-Kovačević, Radioactive ^{32}P, *Tehnika (Belgrade)*, 17: 1041 (1962) (in Serbo-Croatian).
28. O. Jovanović-Kovačevič, and R. Nestorovic, Production of ^{32}P from Neutron-Irradiated P_2O_5, *Tehnika (Belgrade)*, 19: 623 (1964) (in Serbo-Croatian) (English translation JPRS-24590).
29.*S. Milenković, Production and Use of Radioactive Sulfur, *Tehnika (Belgrade)*, 17: 1653 (1962) (in Serbo-Croatian).
30.*J. Stevović and Lj. Jaćimović, Production of ^{131}I, *Tehnika (Belgrade)*, 17: 1449 (1962) (in Serbo-Croatian).
31.*Č. Teofilovski, Process for Making ^{131}I from Dehydrated Telluric Acid, Irradiated in a Reactor, *Chim. Ind. (Paris)*, No. 2025 (1964) (in French).
32. *a.* R. Drašković and S. Vukićević, Production of Radioactive ^{198}Au, *Tehnika (Belgrade)*, 17: 1245 (1962) (in Serbo-Croatian).
b. R. Drašković, J. Čvorić, S. Vukićević, and R. Ilic, New Procedures for Producing Radioactive Colloidal Gold, ^{198}Au, in the Boris Kidrič Institute at Vinča, *Tehnika (Belgrade)*, 20: 228-233 (1965) (in Serbo-Croatian) (English translation JPRS-29258).
33.*S. Kozomara and S. Milenković, Production of High-Specific-Activity ^{51}Cr from K_2CrO_4 Irradiated in a Nuclear Reactor, in press (in Serbo-Croatian).
34.*Dj. Nemoda, Production of ^{60}Co Sources. I. Gamma Radiography Sources; II. Teletherapy Sources, *Tehnika (Belgrade)*, 18: 229, 1009 (1963) (in Serbo-Croatian).
35.*Dj. Nemoda, Preparation of ^{210}Po from Neutron-Irradiated Bi, *Tehnika (Belgrade)*, 19: 428 (1964) (in Serbo-Croatian).

36.*N. Jelić, Production of Controlled ^{60}Co Radiochemical Sources, *Tehnika (Belgrade)*, 19: 819 (1964) (in Serbo-Croatian).

37. N. Jelić, V. Bulović, Lj. Birčanin, and J. Vojnović, Production of ^{204}Tl Sources for Radiography, *Tehnika (Belgrade)*, 18: 1617 (1963) (in Serbo-Croatian) (*Chem. Abstr.*, 61: 3883*b*).

38. Dj. Nemoda and Lj. Birčanin, Radioactive Source Production at Boris Kidrič Institute, *Tehnika (Belgrade)*, 20: 1458-1463 (1965) (in Serbo-Croatian) (English translation JPRS-32260).

39. J. Cvorić, R. Drašković, Dj. Nemoda, and B. Prokić, Chemical and Radiochemical Control of Radioisotopes Used in Medicine, *Tehnika (Belgrade)*, 19: 822 (1964) (in Serbo-Croatian) (*Chem. Abstr.*, 61: 4670*e*).

40.*V. Jovanović and M. Vujević, Control of Sterility of Radioactive ^{131}I, *Tehnika (Belgrade)*, 18: 2005 (1963) (in Serbo-Croatian).

41. I. D. Obrenović-Paligorić and J. D. Čvorić, Separation of Iodide, Iodate, and Periodate by Paper Chromatography, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 14(2): 95-101 (1963) (*Chem. Abstr.*, 59: 14555*b*).

42. N. Cvjetićanin, J. Čvorić, and I. Obrenović, Separation of Monobutyl Phosphate, Dibutyl Phosphate, and Phosphoric Acid and Their Determination in a Tributyl Phosphate-Kerosene Mixture by Paper Chromatography, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 13(1): 35-41 (1962).

43. N. Cvjetićanin and V. Jovanović, Separation of Iodine, As(III), and Te(VI) by Paper Chromatography, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 13(1): 43-51 (1962).

44. V. Jovanović and R. Drašković, Biological Control of Some Radioisotopes for Medical Use, Produced at the Boris Kidrič Institute, *Tehnika (Belgrade)*, 19: 1781-1786 (1964) (in Serbo-Croatian) (English translation JPRS-27762).

45. *a*. R. M. Lemmon, B. Fingerman, and H. Simon, Preparation of Dry K^{14}CN from Ba^{14}CO$_3$, in Chemistry Division Quarterly Report March, April, and May 1957, USAEC Report UCRL-3836, p. 18, June 28, 1957.

b. J. D. Moyer and H. S. Isbell, Preparation and Analysis of ^{14}C-labeled Cyanide, *Anal. Chem.*, 29: 393-396 (1957).

46. V. Jezdić and J. Rajnvajn, Synthesis of Urea-^{14}C and Thiourea-^{14}C, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 12: 127-130 (1961).

47. *a*. D. B. Melville, J. R. Rachele, and E. B. Keller, A Synthesis of Methionine Containing Radiocarbon in the Methyl Group, *J. Biol. Chem.*, 169: 419-426 (1947).

b. L. Pichat, M. Audinot, and J. Monnet, Synthesis of ^{14}C-2-Indole and of β-(^{14}C-2-indolyl) Acetic Acid (heteroauxine), *Bull. Soc. Chim. France*, 21: 85-88 (1954) (in French).

48.*A. Murray III, Sodium Acetate-1-^{14}C, in *Organic Syntheses with Isotopes*, A. Murray III and D. L. Williams (Eds.), Part I, pp. 34-37, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1958.

49. *a*. M. Kleiber, A. L. Blacke, M. H. Brown, and B. M. Tolbert, Propionate as Precursor of Milk Constituents in the Intact Dairy Cow, *J. Biol. Chem.*, 203: 339-346 (1953).

b. M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. F. Yankwich, Acetic Acid-1-^{14}C, in *Isotopic Carbon*, pp. 178-179, John Wiley & Sons, Inc., New York, 1949.

c. J. C. Nevenzel and D. R. Howton, Unsaturated Fatty Acid. IV. Preparation of Oleic-1-^{14}C Acid, *J. Org. Chem.*, 22: 319-321 (1957).

50. F. Kögl, J. Halberstadt, and T. J. Barendregt, Synthesis of L- and D-glutamic Acid-1,2-^{14}C, *Rec. Trav. Chim.*, 68: 387-396 (1949) (in French).

51. W. Sakami, W. E. Evans, and S. Gurin, The Synthesis of Organic Compounds Labeled with Isotopic Carbon, *J. Amer. Chem. Soc.*, 69: 1110-1112 (1947).

52. *a*. V. Jezdić, Synthesis of Thymine-2,4-^{14}C$_2$ and 4-aminothymine-2,4-^{14}C$_2$, *Bull. Inst. Nucl. Sci. "Boris Kidrich,"* 12: 127 (1961).

b.*V. Jezdić, J. Odavić, and N. Vanlić, Synthesis of a Derivative of Uracil-2-^{14}C, in preparation (in Serbo-Croatian).

c.*V. Jezdić and J. Odavić, Synthesis of Orotic Acid-6-^{14}C, in preparation (in Serbo-Croatian).

53. H. L. Otto and M. Winand, The Preparation of Curie Quantities of ^{35}S-labelled Element Sulphur, *Intern. J. Appl. Radiation Isotopes*, 10: 130-131 (1961).

54.*V. Jezdić, M. Skakun, and S. Konstantinović, Synthesis of Some Organic Phosphorus Insecticides Containing ^{32}P and ^{35}S (Diptereks-^{32}P, Malathion-^{32}P, Malathion-^{35}S) in preparation (in Serbo-Croatian).

55. Yu. V. Markova, A. M. Pozharskaya, V. I. Maimind, T. F. Zhukova, N. A. Kosolapova, and M. N. Shchukina, Synthesis of Physiologically Active Compounds Labeled with ^{35}S, *Dokl. Akad. Nauk SSSR*, 91: 1124-1132 (1953) (in Russian).

56.*Z. Dizdar (Ed.), *Radioisotope Catalog*, 2nd ed., Boris Kidrič Institute of Nuclear Science, Vinča, 1964 (in Serbo-Croatian) (but see Radioactive Isotopes, USAEC file No. NP-15039, in English).

57. P. Strohal, Cyclotron Production of Isotopes, *Nukl. Energ.*, 2(2): 10-13 (1965) (in Serbo-Croatian).

58. D. Keglević, Synthesis and Use of ^{14}C-labeled Compounds, *Nukl. Energ.*, 2(2): 14-15 (1965) (in Serbo-Croatian).

59. J. Gligorijević, Use of Radioisotopes in Veterinary Medicine, *Nukl. Energ.*, 2(2): 16-22 (1965) (in Serbo-Croatian).

60. *a*. Proceedings of the Third Yugoslav Symposium on the Application of Radioactive Isotopes and Radiation in Industry, Herceg Novi, May 1965 (in Serbo-Croatian) (CONF-650565; *Nucl. Sci. Abstr.*, 20: 19128) [summarized by Z. Dizdar in *Nukl. Energ.*, 2(3): 27 (1965) (in Serbo-Croatian)].

b. The Third Yugoslav Symposium on the Application of Radioactive Isotopes and Radiation in the Economy, *Tehnika (Belgrade)*, 20: 637-644 (1965) (in Serbo-Croatian) (English translation JPRS-30770).

61. Z. Draganic and M. Kosanic, Irradiation Possibilities in the 2-kc ^{60}Co Radiation Unit at the Boris Kidrič Institute at Vinča, *Tehnika (Belgrade)*, 20: 1852-1857 (1965) (English translation JPRS-32813).

Radioisotopes in Australia

62. *a*. Australian Atomic Energy Commission, *The Technological Use of Radiation*, Conference

Proceedings, Sydney, Australia, 1960, Grant and Walker, Pty. Ltd., Leichhardt, N.S.W.

b. Australian Atomic Energy Commission, 13th Annual Report, 1964–1965, pp. 61-70.

c. Catalogue of Radioisotopes, Radioactive Preparations, Special Purpose Sources, Service Irradiations (and) Special Services. Overseas edition, March 1965, AAEC, Coogee (USAEC file No. NP-15575).

63. *a.* J. G. Clouston, W. R. Ellis, U. Engelbert, J. N. Gregor, G. L. Miles, and J. S. Watt, Some Recent Australian Developments in the Application of Radioisotopes and Radiation Sources, *Atompraxis*, 11: 208-214 (1965).

b. G. L. Miles and C. N. Watson-Munro, The Design and Construction of Research Facilities for a Power Development Program, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses Atomic Energy, Geneva, 1958*, Vol. 1, pp. 102-110, United Nations, New York, 1958.

c. K. F. Alder and W. H. Roberts, The Australian High-Temperature Gas-Cooled Reactor Research Project, Australian Report AAEC/E-122, July 1964.

64. Australian Designed Gamma Radiation Facility, *At. Energy Australia*, 7(1): 23 (1964).

65. P. A. Wills, Some Effects of Gamma Radiation on Several Varieties of Tasmanian Potatoes. I. Storage Problems; II. Biochemical Changes, *Australian J. Exptl. Agr. Animal Husbandry*, 5(18): 282-295 (1965).

66. *a.* P. A. Wills, Use of Gamma Radiation for Quarantine Control of Imported Edible Beans, *Nature*, 207: 100-101 (1965).

b. P. A. Wills, Some Effects of Gamma Radiation on *Phaseolus vulgaris* Seeds, Australian Report AAEC/TM-263, August 1964.

67. R. D. Brock, Ionising Radiations and Plant Improvement, *At. Energy Australia*, 8(2): 18-21 (1965).

68. *a.* Production of Medical Radioisotopes by the AAEC, *At. Energy Australia*, 8(4): 24-26 (1965).

b. J. G. Clouston, Industrial Applications of Radiation, in *Atomic Power: A Review*, Symposium Proceedings, Sydney, 1963, University of New South Wales, Sydney.

c. G. S. Murray, Industrial Sterilization by Gamma Radiation, *At. Energy Australia*, 5(4): 2-6 (1962).

d. W. Woods, Cobalt Beam Therapy Units: Their Place in the Management of Cancer, *At. Energy Australia*, 8(1): 18-21 (1965).

69. AAEC Radiography Sources, *At. Energy Australia*, 7(4): 12 (1964).

70. C. M. Gray, Gamma Radiography at New Zealand Geothermal Steam Power Station, *At. Energy Australia*, 7(3): 7-11 (1964).

71. Non-destructive Testing, *At. Energy Australia*, 7(2): 13 (1964).

72. *a.* J. S. Watt, Gamma-Ray Excited X-ray Sources, *Intern. J. Appl. Radiation Isotopes*, 15: 617-625 (1964) (same as AAEC/TM-226, 1963) (Suppl. 1 issued 1965).

b. J. S. Watt, Design and Applications of Gamma-Ray Excited X-Ray Sources, *At. Energy Australia*, 8(2): 6-9 (1965).

73. J. A. Hope and J. S. Watt, Alloy Analysis and Coating Weight Determination Using Gamma-ray Excited X-ray Sources, *Intern. J. Appl. Radiation Isotopes*, 16: 9-14 (1965).

74. J. N. Gregory, Some Recent Developments in the Application of Radioisotope Techniques in Australia, in *Radioisotopes in the Physical Sciences and Industry, Conference Proceedings*, Copenhagen, 1960, Vol. 1, pp. 415-431, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/20).

75. *a.* J. S. Watt, Some Recent Applications of Short-Half-Life Radioisotopes in Australia, in *Production and Use of Short-Lived Radioisotopes from Reactors*, Conference Proceedings, Vienna, 1962, Vol. 1, pp. 343-355, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/64).

b. D. H. Pilgrim and K. K. Watson, The Application of Radioisotope Techniques to Water Engineering Investigations, *J. Inst. Engrs., Australia*, 37: 175-184 (1964).

76. W. R. Ellis, Measurement of Water Flow in an Air-Conditioning Unit by a Radioisotope Method, *J. Inst. Engrs., Australia*, 37(4-5): 135-136 (1965).

77. B. L. Campbell and W. R. Ellis, The Development of Oil-Soluble ^{198}Au Compounds for Industrial Radiotracing, *Intern. J. Appl. Radiation Isotopes*, 16: 257-259 (1965).

78. D. E. Hull, The Total-Count Technique: A New Principle in Flow Measurement, *Intern. J. Appl. Radiation Isotopes*, 4: 1-15 (1958).

79. J. T. G. Andrew, W. R. Ellis, B. W. Seatonberry, and W. A. Wiebenga, The Use of Radioisotopes as Ground-Water Tracers in the Burdekin Delta Area of North Queensland, Australia, Australian Report AAEC/E-137, May 1965.

80. B. L. Campbell, Sediment Research in Australia, *At. Energy Australia*, 7(4): 13-17 (1964).

81. B. L. Campbell, An Improved Technique for Labelling Sand with ^{198}Au, *Intern. J. Appl. Radiation Isotopes*, 14: 286-287 (1963).

82. B. R. D. Gillings, The Use of Radioisotopes in Dental Research, *At. Energy Australia*, 8(4): 17-23 (1965).

83. R. A. Fookes, J. S. Watt, and J. A. Warburton, A Radioisotope Technique for Tracing Air Movements in Clear Air and in Clouds, *Nature*, 196: 328-329 (1962).

84. M. Thackray, Evidence for the Beta-Gamma Transition Point in Sulphur from Low-Temperature Solubility Measurements Using ^{35}S, and Its Relevance to the Theory of Interface Reactions in Solids, *Nature*, 210: 674 (1964).

85. W. R. Ellis and B. W. Seatonberry, A Radioisotope Method for Locating Points of Entry of Carbon Monoxide into the Cabin of an Aircraft, *Intern. J. Appl. Radiation Isotopes*, 17: 81-84 (1966).

Some other pertinent publications announced by the AAEC are:

J. G. Clouston, Irradiation Plants for Industrial Processing, *Food Technol. Australia*, 16(1): 16 (1964).

J. G. Clouston and D. F. Sangster, Sterilising with Ionising Radiation, Suppl. No. 18, *Australian J. Pharm.*, 45(534): (1964).

A. Hughes and P. A. Wills, Some Effects of Ionising Radiation on Certain Substances Used in Eye-Drops, Suppl. No. 9, *Australian J. Pharm.*, 44(525): (1963).

R. M. Cowdroy and P. S. Davis, Low-Level Radiochemistry Laboratory, *Arch. Australia*, 53(1): 120 (1964).

J. G. Clouston and D. F. Sangster, Chemical Processing with High-Energy Radiation, *Australian Chem. Process. Eng.*, 18(4): 18-25 (1965).

G. C. Lowenthal, Radioisotope Standardisation, *Australian Phys.*, 2(5): 77-78, 85 (1965).

D. R. Davy, Absolute Calibration of Radioactive Neutron Sources, Australian Report AAEC/TM-288, 1965.

Section

VIII

Isotopes and Radiation Technology

Miscellaneous Items of Interest

Conferences

Georgia Meeting Emphasizes Evaluation of Commercial Aspects of Wood Plastics

A meeting to evaluate and to emphasize the commercial potential of wood–plastic combinations (WPC) for Georgia's industries was held Mar. 11, 1966, in Atlanta's Commerce Building. The meeting, which was sponsored by the Georgia Department of Industry and Trade, the Georgia State Chamber of Commerce, and the Engineering Experiment Station of the Georgia Institute of Technology, was directed not to the technical aspects of WPC but to an evaluation by producers, industrialists, and businessmen to give them an opportunity to discuss the economic possibilities and advantages that the new products could provide Georgia's industry. Although Georgia is one of the major producers of softwoods among the southern states, it also produces some hardwoods. A technical brochure* prepared by the Pan American Consulting Corporation had been sent to prospective attendees prior to the meeting.

Buford B. Ruhl, President of the Pan American Consulting Corporation and an avid proponent of the fledgling WPC industry, was chairman of the meeting.

Justin L. Bloom, Chief, Radiation Applications Branch, U. S. Atomic Energy Commission (AEC), discussed plant and materials cost with emphasis on radiation sources and source characteristics. Both ^{60}Co and ^{137}Cs can be used as sources; however, technical and economic evaluations of various factors—cost of the activity, energy and amount of radiation, encapsulation cost, and half-life—must be considered in the design of commercial radiation sources. In the production of WPC, the cost of radiation is relatively small; the largest single cost is that of the monomer.

Lawrence Barrett of the American Novawood Corporation announced that their first run with the new cobalt irradiator was completed at 1:30 a.m. on Mar. 10, 1966. Samples of this initial run of the world's first WPC commercial production facility were given to each person at the meeting. American Novawood had previously used two reactors for the development work on production of WPC. The plant facilities can process methyl methacrylate, styrene–acrylonitrile, and acrylates, among others. Barrett emphasized that Novawood is now a production item, produced in a plant financed exclusively with private capital.

A. O. Burford of the Lockheed-Georgia Company said that their plant capacity is 250,000 bd ft/year and that methyl methacrylate monomer is used exclusively. Wood plastics are more expensive than untreated wood products, and the cost depends on the amount of plastic in the wood. Development prices at Lockheed are about $3.15/bd ft. (Recent information indicates the current price for WPC is now about $1.50 to $2.00/bd ft of lumber depending on type of wood, quantity, and other factors.)

William Bell, also of Lockheed-Georgia Company, stated that effort should be focused on the market place; there are now 200 products under consideration, and many more possibilities exist.

W. H. Burrows of the Industrial Products Branch, Georgia Institute of Technology, stressed that WPC are new materials and should not be considered woods, plastics, or improvements of these; new products should be created from WPC. The number of combinations of species of wood, monomers, loading levels, irradiation times, dye combinations, and other variables could reach one-half mil-

*Pan American Consulting Corporation, New Wood–Plastic Combination Materials, Chamblee, Ga., 1966.

lion, and these variables need to be evaluated.

B. W. Carmichael, Research Division, Georgia Department of Industry and Trade, gave three possibilities for WPC: substitutes for woods, substitutes for plastics, and completely new materials. The national average of increase in value of wood products from stumpage to finished products is 25-fold, but Georgia's average is only 10-fold. If Georgia's industry could bring the increase in value to the national average, over 30,000 new jobs would be provided within the state. Carmichael estimated that over 20% of all Georgia industries could use WPC in one way or another.

J. H. Nutter, Jr., Georgia Department of Industry and Trade, urged Georgia manufacturers to take advantage of these new products to bring this new industry into the state, which has a great asset in the Lockheed-Georgia Company's facility near Atlanta.

J. E. Machurek, Division of Isotopes Development (DID) AEC, stated the AEC's belief that a practical demonstration of the WPC process (as well as one for radiation processing in the production of polyethylene) would be worthwhile. Accordingly the Commission is soliciting expressions from industrial firms, groups of firms, and others concerning the types of AEC assistance that would be required for industry to undertake construction and operation of a WPC demonstration facility. The primary objective of the AEC participation would be to study and evaluate processing and economic factors on a near-commercial scale. With authorization, the AEC would consider providing assistance, at minimum cost to the government, under a cooperative agreement. The AEC feels that such a program would encourage widespread industrial application of radioisotopes and radiation.

Machurek said that one form of economic assistance by the AEC to such a program might be the provision of a radiation source and technical assistance without cost. The degree of participation in management and development planning by each party would depend on the relative portion of capital provided by each. Patent rights, associated commercial production, if any, and other benefits would be subject to negotiation with the AEC.

A discussion period followed the formal presentations. Economics of production, degree of AEC participation, commercial promotion, and volume of production were of primary concern. The general attitude of wood-product manufacturers at the meeting might be described as one of cautious optimism. (R. E. Greene)

AEC–USAF Review "Isotopes in Aerospace"

The recent symposium on radioisotope applications in aerospace held Feb. 15–17, 1966, in Dayton, Ohio, was sponsored by the Air Force Flight Dynamics Laboratory of the U. S. Air Force and the Division of Isotopes Development of the U. S. Atomic Energy Commission. Approximately 460 persons attended 12 sessions that covered both unclassified and classified applications. The well-organized meeting reflected the thorough planning of the various chairmen and committees—particularly the work of the symposium deputy chairmen, Paul Polishuk and Jack Dempsey. Only brief mention of the subject matter is included here, since the proceedings of the meeting are to be published by the Instrument Society of America sometime after July 1, 1966.

The first two unclassified sessions, on Tuesday, dealt with radiation detectors and electronics, with the first two papers reviewing, respectively, "Progress in Nuclear Electronics" and "Nuclear Electronics for Aerospace Applications." Other topics dealt with gas counters, a state-of-the-art review of neutron detection, ruggedized multiplier phototubes, and contoured and nuclear particle semiconductor detectors.

In an "Information and Safety" session, Oak Ridge National Laboratory's (ORNL) new Isotopes Information Center was discussed (see this issue of *Isotopes and Radiation Technology*, page 179). This was followed by a consideration of the applications of radioisotopes in areas of federal interest such as the military and space programs. In a paper by Paul Tompkins of the Federal Radiation Council, the radiological health problems associated with the use of radioisotopes were discussed. It was felt by some attendees that the presentation was perhaps a little too pessimistic. The last three papers covered (1) the Gemini spacecraft environmental control system, which uses a radiological gas analyzer to detect the buildup of metabolic CO_2 from the astronauts; (2) an instrument using the radioactive clathrate techniques to detect certain reactive atmospheric gases in the ppm range (e.g., halogens, SO_2,

NO, O_3, and amines); and (3) the ORNL safety testing program, which is directed toward obtaining information that can be used by source manufacturers, standards groups, and regulatory agencies to design and specify sources and shipping containers that are consistent with safety requirements.

The Wednesday morning session on the measurement of atmospheric data parameters using isotopes included such topics as the measurement of atmospheric density by gamma backscatter, altitude measurement and terrain identification with pulsed X rays, the use of alpha-excited fluorescent X rays for gas and solid composition measurements, and the use of $^{95}Zr-^{95}Nb$ and ^{114m}In for studying the feasibility of continuous measurement of the ablation of a spacecraft heat shield.

A parallel Wednesday morning session on the use of radioisotopes in ranging and guidance covered several types of problems and potential applications: (1) ^{60}Co in a sensitive tracing system for measuring missile and rocket trajectories during the lift-off phase; (2) ^{241}Am, ^{137}Cs, and ^{85}Kr in a helicopter close-order formation-keeping system; (3) ^{60}Co and ^{137}Cs for measuring direction and distances between aircraft, ships, and other objects; (4) gamma emitters for prompt measurement of "miss distance" during missile flight past a target; (5) a study of gamma radar interaction phenomena; and (6) a consideration of army-aircraft-related problems where the application of radioisotopes may be helpful, e.g., power plants and trains, fuel measuring and quality control, altitude sensing, target detection and/or marking, and communications.

Several papers in one of the Wednesday afternoon sessions were related to the use of radioisotopes in the measurement of fuel–oxidizer properties and quantity. Three of these dealt with systems that would allow accurate in-flight measurement of fuel reserves under conditions of zero gravity and without regard to attitude. One paper considered a continuous oil-quantity gaging system from the same standpoint. Another discussion related to a ^{90}Sr system for estimating the density of two-phase hydrogen. The next two involved, respectively, the use of a backscatter technique to measure liquid-hydrogen creep in a vent line and an investigation to develop and determine the feasibility of a nuclear system for measuring local densities of cryogenic liquids. The last paper in the session related to the development of a mathematical model of a fuel-gaging system to permit optimization of system configurations by computer techniques.

The first paper in the parallel session, on machine and isotopic radiation sources, discussed the use and advantages of such isotopes as ^{90}Sr and ^{147}Pm to simulate space-radiation environment at any specified altitude. This was followed by a discussion of ^{85}Kr "Kryptonates" (see this issue of *Isotopes and Radiation Technology*, page 206), with emphasis on methods of preparation, properties, and uses in temperature profile histories of engine turbine blades, in hazardous or toxic missile-gas analysis, in oxidation and corrosion studies, and in friction and wear studies. This was followed by a description of the methods used in the fabrication of low-energy gamma sources made from ^{144}Ce, ^{109}Cd, ^{241}Am, ^{133}Xe, ^{57}Co, ^{151}Sm, ^{55}Fe, and ^{147}Pm, and bremsstrahlung and X-ray sources from $^{3}H-Ti$, ^{99}Tc, $^{147}Pm-Al$, $^{147}Pm-Mo$, $^{147}Pm-Sn$, $^{99}Tc-W$, and $^{147}Pm-U_3O_8$.

A 50-lb 150-kev flash X-ray system complete with dry-film processing was the subject of the next paper. Such a combination of high output power with reliability and small size makes these devices suitable for stop-motion radiography and radiation-effects studies for aerospace applications. The next two papers in the radiation-sources section covered (1) isotopic neutron sources, including spontaneously fissioning heavy elements; and (2) discharge type (broad neutron-energy spread) and pulsed-beam type (ideal energy resolution) pulsed neutron sources with time-average neutron production of 10^{10} to greater than 10^{11} n/sec for applications in nuclear engineering, activation analysis, materials analysis, velocity measurements, and inspection. The final paper reviewed a study performed to define the relative advantages and limitations of radioisotope and machine sources of radiation for typical aerospace applications.

One of the Thursday morning sessions included six papers dealing with nondestructive techniques using radioisotopes. These papers dealt with the use of a beta-radiation probe to detect corrosion beneath a protective polymeric coating; a radioisotope inspection system to measure residual flux on automatically processed electronic-circuit boards, using a large-area plastic-scintillator beta detector; the use of isotope radiography sources for inspection

of the interior of aircraft jet engines; a consideration of some unusual sources such as ^{125}I and beta-excited X-ray sources using ^{85}Kr, ^{147}Pm, and ^{90}Sr, for radiographic applications, and reference to the usefulness of neutron radiography for imaging hydrogenous materials; the use of a low-cost neutron activation technique for analyzing metallic deterioration products filtered out of aircraft hydraulic systems; and an autoradiographic technique for studying crack propagation and failure mechanics in plastics and composite materials for aerospace application.

The final unclassified session, also on Thursday morning, was entitled "Advanced Isotope Applications." It covered a rather broad spectrum and included papers on luminous light sources energized by ^{85}Kr; some applications of the Mössbauer effect in aerospace; the feasibility of using an alpha-backscatter technique for lunar-surface analysis; two papers on analysis of elements (such as iron, silicon, oxygen, magnesium, aluminum, sodium, potassium, and calcium) based on the gamma rays resulting from inelastic scatter of 14-Mev neutrons generated in a 15-lb instrument suitable for planetary surface analysis; the "Gulliver" experiment using radioisotope tracer techniques to establish the existence of both extraterrestrial and terrestrial microorganisms by the monitoring of labeled gas expired as a result of metabolism; and, finally, the use of nuclear radiation, from either fission or radioisotopes, to provide primary power for pumping lasers.

The Symposium also included three classified sessions — one on "Isotope Applications," and two on "Heat Source Applications for Electric Power, Propulsion, and Life Support."

In conjunction with the meeting there were a number of exhibits and displays, primarily by groups participating in the meeting.

(P. S. Baker)

AEC Activities

Isotopes Program Outlined in AEC Report and E. E. Fowler Testimony

Major advances and future emphasis of the AEC's isotopes development program, recently reviewed in two documents, are summarized here.

The overall AEC program was presented in its annual report,[1] which covers developmental, promotional, regulatory, and adjudicatory activities of the Commission for January–December 1965.

E. E. Fowler, director of the DID, in formal testimony[2] before the Joint Committee on Atomic Energy (JCAE), discussed the DID Fiscal Year 1967 request.

Financial–operational aspects of the DID program have also been discussed by other publications[3,4] and previous issues of *Isotopes and Radiation Technology*. Table VIII-1 summarizes AEC development funds for the past year and compares these with future requests.

Table VIII-1 ISOTOPES DEVELOPMENT PROGRAM OPERATING FUNDS, FY 1965–1967

(Figures Are in Thousands of Dollars[5,5a])

Program	FY 1965, actual	FY 1966, estimates	FY 1967, estimates to Congress
Radioisotope Technology Development	1,120	1,400	1,400
Thermal Applications of Radioisotopes	141	200	400
Isotopic Power and Heat Source Fuels	3,084	4,900	7,780
Radioisotope Production and Separations Technology	1,665	1,600	1,700
Process Radiation Development	1,721	1,800	1,800
Radiation Preservation of Foods	1,101	1,700	1,700
Total	8,832	11,600	14,780

The requested 1967 operating funds are up 27% from FY 1966, an increase of $3.2 million. A major part of this increase ($1.8 million) is attributable to expected research and development work on isotopic power and heat-source fuels. The budget also allows for $3.8 million for supporting equipment and $3.0 million for the construction of an Alpha Fuels Environmental Test Facility at Mound Laboratory.

About one-half of the FY 1967 budget is intended for development of radioisotopic power and heat-source fuels. Another one-third of the budget is intended for work leading to industrial application of radioisotopes. Several AEC–industry projects, jointly financed, are planned. In 17 projects, development costs are shared by AEC and interested federal agencies.

Radioistope Technology Development

This program is aimed at developing new ideas and concepts for broadening the technological base for expanded use of radioisotopes and at encouraging, through demonstration projects, the use of technology by government agencies, industry, and others. Effort is divided into two principal categories: basic technology development and systems engineering applications. About one-sixth of the Radioisotope Technology Development FY 1967 budget is devoted to the former effort. The rest is slated for engineering research and development of specific systems.

Fowler mentioned three applications under development and planned for continuation in FY 1967: a helicopter formation-keeping system, an aircraft liquid-fuel gage, and an activation analysis system for industrial quality control.

The 1965 AEC report describes a number of isotopic devices that moved from development to application stage and radioisotope-instrumented systems that solved various problems of direct government and industry interest. Several projects were continued into 1966 for solving problems in snow and watershed management: automatic calibration of high-head turbines, determination of source of water loss in large reservoir sites, and pollution control of paper-waste discharge into rivers.

HELICOPTER FORMATION-KEEPING SYSTEM

The U. S. Navy and AEC are developing an isotopic sensor system to permit helicopters to fly in formation under restricted visibility conditions. A prototype was successfully demonstrated on land in FY 1966, and a flight test is planned at the Naval Development Center, Philadelphia, in FY 1967.

AIRCRAFT LIQUID-FUEL GAGE

The U. S. Air Force and AEC are working on a nuclear gage that will give continuous, precise measurement of the consumption of fuel on board military aircraft. Excess fuel is loaded on aircraft to compensate for the margin of error inherent in presently used gages. An already-developed nuclear oil gage is being installed in military fighter planes; zero-gravity spacecraft propellant gages are reaching the hardware stage under AEC, military, and National Aeronautics and Space Administration (NASA) sponsorship.

ACTIVATION ANALYSIS FOR INDUSTRIAL QUALITY CONTROL

The project aims to permit continuous analysis of the constituents of raw materials in the manufacturing process. In FY 1966 a pilot plant was placed in operation which enables interested companies to ship large quantities of solid materials, such as coal, metal ores, and flour, to the plant for demonstration of the feasibility of this process. In FY 1967 a second pilot plant is planned. This will be designed to demonstrate the applicability of this method to liquid raw materials under continuous flow. More than one-half the cost of this development effort is being borne by industry.

SELECTED STUDIES AND SYSTEMS IN 1965–1966

Helium-3 Activation Analysis. A new technique in activation analysis using nuclear reactions resulting from accelerated ^3He ions has been further perfected by General Atomic Division of General Dynamics Corporation, San Diego, Calif. The high sensitivity of this technique, especially for the measurement of oxygen and carbon in metallic surfaces, has drawn considerable interest from industry. Oxygen determinations have been made on stainless steel, tantalum, and platinum. Measurements of oxygen in stainless steel heated to high temperatures have revealed the usefulness of the method in degassing studies.

Alpha-Excited X Rays. Parametrics, Inc., Waltham, Mass., is working on the generation of monoenergetic, characteristic X rays of various materials, without the usual bremsstrahlung radiation present with beta irradiation (see page 214 of this issue of *Isotopes and Radiation Technology*). The X-ray yields of aluminum, titanium, copper, and vanadium have been measured and found to be significant. Spectra have been obtained for targets of all four elements, and examination of the first three indicates that such sources can be used for applications of X-ray fluorescence and absorption analysis. Investigations are under way with other agencies to determine the feasibility of applying this technique to lunar analysis and to analysis of wear products in aircraft engine oils.

Stable-Isotope Measurement. A project at Tracerlab, Inc., Waltham, Mass., is directed toward the development of a comparatively inexpensive microwave spectroscope to measure

stable isotopes, with very high sensitivity. In some instances it is desirable to employ stable isotopes as tracers rather than to use radioactive isotopes, as in medical diagnostic procedures in children. A prototype, which operates in the millimeter wavelength range, has been completed to measure such isotopes as ^{15}N with the highest possible sensitivity, in the temperature range of −80 to 300°C. The console unit, when completed, will be the size of a desk top and easily transportable. The spectrometer was chosen by *Industrial Research Magazine* as one of the 100 most significant developments in 1965.

Gold Detector. A radioisotope-activated narrow-band X-ray gold detector, built by Tracerlab, Inc., has generated much international interest by gold prospectors, mine owners, and customs officials (see page 216, this issue).

Ocean-Bottom Measurements. Tests conducted by the U. S. Navy Oceanographic Office at Panama City, Fla., with an ocean-bottom sediment-density meter exceeded expectations (see page 216, this issue). The completely self-contained device was developed by Lane-Wells Co., Houston, Tex., and is to be modified to permit measuring the moisture content of sediments by a neutron absorption–scattering technique.

Snow–Water Management. A long-term project is continuing with the U. S. Forest Service to develop a snow–water management-control system for the state of California. Efforts include the development of automated telemetry systems to transmit isotopic measurement of snow characteristics data and the evaluation of hexadecanol for retarding evaporation of water from the snow pack. The snow-measuring unit consists of a portable source–detector employing the backscatter from neutron and gamma sources to determine snow characteristics in half-inch vertical increments with an accuracy of 95% or better. The hexadecanol study uses radioisotope tracers to measure the concentration and distribution of the microscopic covering of hexadecanol on the snow and to determine the efficiency of the protection from evaporation. [Radiosnow gages were reviewed in *Isotopes and Radiation Technology*, 2(1): 41-47 (1964).]

Turbine Rater. An isotopic turbine-rating technique, previously developed for low-head turbines (water drop of less than 200 ft), of the type found in the Tennessee Valley Authority complex, is now being extended to high-head turbines by the U. S. Bureau of Reclamation, Denver, Colo. The technique uses the isotope-dilution principle (see page 217, this issue).

Thermal Applications of Radioisotopes

The funding level for this program in FY 1967 reflects increased interest in space and marine applications by the military services and NASA. Fowler described two specific projects: a water recovery system for spacecraft and a swimsuit heater.

WATER RECOVERY SYSTEM FOR SPACECRAFT

Two projects are planned in FY 1967 for developing radioisotope-based water recovery systems; one of these will be in cooperation with the U. S. Air Force.

SWIMSUIT HEATERS

A cooperative project is in progress with the U. S. Navy to develop a radioisotope source to supply heat to underwater swimmers. The heat would be transmitted through a fluid and vein-like tubes embedded in the swimsuit. A prototype heat source and exchanger is planned for development in FY 1967.

SELECTED STUDIES AND SYSTEMS FOR 1965–1966

Survey of Hydrospace Uses. Aerojet-General Corporation, San Ramon, Calif., interviewed several hundred people in government, industry, and academic institutions, to determine potential hydrospace applications of radioisotopes. These included underwater sound generation, instrument electric-power supply, propulsion for small submersibles, electric and thermal power for undersea platforms, and small heat sources. Several of these concepts are being explored, and in some cases, cooperative programs are under way with potential users.

Submersible Propulsion Engine. A design study is being conducted by Aerojet-General Corporation to integrate an isotopic heat source with a turbine for propulsion of small undersea craft. The project includes conceptual design, detailed program planning, and initial research and development of a proof-of-principle engine for specific hydrospace applications. Numerous engine cycles and power-conversion concepts have been studied. A Rankine-cycle turbine

using Dowtherm A (an organic material) as a working fluid in a direct, single-loop, regeneration system and a ^{60}Co boiler is proposed.

Small Spacecraft Thrusters. TRW—Space Technology Laboratories, Inc., Redondo Beach, Calif., designed a radioisotope capsule to heat the catalyst bed of a monopropellant hydrazine engine. A Nuclear Isotope Monopropellant Hydrazine Engine (NIMPHE), to be used for propulsion of unmanned space vehicles, is capable of an unlimited number of startups and delivers excellent propellant performance over a wide range of duty cycles. The catalyst bed, however, is not capable of initiating hydrazine decomposition at ambient temperatures and must be heated. The radioisotope makes it possible to use a catalyst with unmatched physical and chemical properties at high temperature. The engine has had a test run of 2000 starts using an electric heater to simulate an isotope heat source.

Space Life-Support Systems. The AiResearch Mfg. Div. of the Garrett Corp., Los Angeles, Calif., evaluated the applications of isotopes for life-support systems in manned spacecraft. These included water recovery, carbon dioxide removal, oxygen recovery, heating, cooling, and particle removal within the spacecraft. Radioisotope heat sources were evaluated against conventional sources of power. The results indicate that the direct use of isotopic thermal energy offers distinct advantages over electricity-to-heat conversion systems for certain missions.

In a cooperative program with the U. S. Air Force, AiResearch designed an integrated water system for recovering potable water from urine, condensate, and wash water and for heating, cooling, and dispersing the water and maintaining it pasteurized. Plutonium-238 is being evaluated by Mound Laboratory and ^{147}Pm by Pacific Northwest Laboratory as heat sources for this purpose.

Isotopic Power and Heat-Source Fuels

A number of heat-producing isotopes are of major interest for space and terrestrial applications in this program. The more important ones are produced directly by neutron addition reactions in nuclear reactors—^{238}Pu, ^{242}Cm, ^{244}Cm, ^{60}Co, and ^{210}Po. Fission-produced isotopes also are important; ^{90}Sr is used most often.

A major increase in efforts planned for FY 1967 will be on materials and fuel-forms research and development. Plutonium-238 and ^{210}Po processing will be increased at Mound Laboratory, and megacurie quantities of ^{147}Pm and multikilowatt(th) quantities of ^{60}Co will be produced at Pacific Northwest Laboratory and at the Savannah River Plant, respectively. These materials, together with 3 kg of ^{244}Cm being produced at SRL, to become available during FY 1967, will be processed into fuel forms for evaluation. Some of the areas requiring continued investigation are:

1. Fuel-form stability at temperatures between 1000 and 2000°C
2. Physical characteristics, stability, and performance of encapsulating materials in these temperature ranges
3. Physical and chemical compatibility of the fuel forms with liner materials to assure adequate containment of the fuel
4. Fuel-capsule designs commensurate with the temperature extremes to which the capsules will be exposed
5. Nondestructive testing techniques adequate to assure the integrity of the encapsulated fuels under simulated conditions of use

Particular fuel forms and capsules will be developed for several missions. Among these are the SNAP-27 Apollo Lunar Survey Experimental Package (ALSEP), the SNAP-19 weather satellite (NIMBUS-B), and an anticipated classified Department of Defense (DOD) space project.

SELECTED STUDIES FOR 1965–1966

Both space and terrestrial SNAP devices have been reviewed in *Isotopes and Radiation Technology*, and Tables VIII-2 and VIII-3 list some of the characteristics and the status of these units.

SNAP-27. Initiated in 1965, this program is aimed at the design, development, test, and demonstration of a 50-watt ^{238}Pu-fueled power supply to be used by NASA in the Apollo program. General Electric's Missile and Space Division at Valley Forge, Pa., is developing this device.

Other SNAP Studies. A number of other projects are underway:

1. High-Powered Long-Life Units. In December 1965 the AEC initiated generator engineer-

Table VIII-2 LAND AND SEA SNAP UNITS

Designation	Use	Power, watts	Weight, lb	Isotope	Minimum design life, years	Remarks
Undesignated (Sentry)	Axel Heiberg weather station	5	1680	^{90}Sr	2	Installed in Arctic, August 1961; removed October 1965
SNAP-7A	Navigational buoy	10	1870	^{90}Sr	2	Test at Coast Guard's Curtis Bay, Md., facility, January 1964
SNAP-7B	Fixed navigational light	60	4600	^{90}Sr	2	Installed in Chesapeake Bay, May 1964
SNAP-7C	Land weather station	10	1870	^{90}Sr	2	Installed in Antarctica, February 1962
SNAP-7D	Floating weather station	60	4600	^{90}Sr	2	Installed in Gulf of Mexico, January 1964
SNAP-7E	Ocean-bottom beacon	7.5	6000	^{90}Sr	2	Installed in Atlantic Ocean, July 1964
SNAP-7F	Navigational equipment on oil rig	60	4600	^{90}Sr	5	Installed in Gulf of Mexico, June 1965; removed October 1965
SNAP-15	Small electronic apparatus	0.001	<1	^{238}Pu	5	Operational test of fueled prototypes
SNAP-21	Advanced undersea	10–60	500*	^{90}Sr	5	Prototype generator fabrication and testing started, December 1965
SNAP-23	Advanced terrestrial	25–200	900†	^{90}Sr	5	Design and component development completed, December 1965

*For the 10-watt version. †For the 60-watt version.

ing studies to determine the feasibility of 250- to 300-watt plutonium- and strontium-fueled thermoelectric power systems that would be particularly suitable for long-life space applications.

2. Polonium Power System. In September 1965 the AEC initiated preliminary engineering, design, and integration studies on a polonium-fueled thermoelectric generator for possible application in a DOD mission. This generator[5a] has been designated SNAP-29.

Table VIII-3 SPACE SNAP UNITS

Designation	Use	Power, watts	Isotope
SNAP-3	Navigational satellites (DOD)	2.7	^{238}Pu
SNAP-9A	Navigational satellites (DOD)	25	^{238}Pu
SNAP-11	Experimental devices	20–25	^{242}Cm
SNAP-19	NIMBUS-B	30	^{238}Pu
SNAP-27	ALSEP	50	^{238}Pu

Large Heat-Source Studies. Large radioisotope heat sources using ^{244}Cm, ^{238}Pu, and ^{210}Po which are compatible with thermoelectric or dynamic conversion devices are of interest as subsystems of manned and unmanned space electric-power systems which provide 1 to 10 kw of electricity. As a first step in the AEC's consideration of such power systems, two parallel preliminary design and safety studies were conducted: one by Atomics International, Canoga Park, Calif., the other by General Electric's Missile and Space Division. The final reports are classified and are available to qualified individuals through C-92a distribution from DTIE, P. O. Box 62, Oak Ridge, Tennessee 37830.

SNAP-23. The Minnesota Mining & Manufacturing Co. is conducting the first phase of this effort—design and component development. Results have indicated that the second phase—prototype generator fabrication and testing—could be started during 1966, with a fueled 60-watt prototype being made available in 1967 for environmental testing.

SNAP-21. An electrically heated prototype 10-watt generator was fabricated and successfully tested by the Minnesota Mining & Manufacturing Co., St. Paul, Minn. A fueled prototype 10-watt unit was readied for testing under operating environments in 1966. Increased efficiency, reliability, and a substantial reduction in size and weight is expected to be achieved through the use of newly developed and proved thermoelectric materials, higher hot-junction temperatures, improved thermal insulation, and an improved design. As an example, the 7.5-watt SNAP-7E undersea generator weighed 6000 lb; a 10-watt SNAP-21 unit is expected to weigh about 500 lb.

SNAP-19. In February 1965 two electrically heated SNAP-19 prototype generators were

delivered by the Martin Co. to NASA's Goddard Space Flight Center (Greenbelt, Md.) where they were subjected to electrical performance and electrical integration tests based on NIMBUS-B weather-satellite specifications. In November, two SNAP-19 generators were shipped to General Electric Company (Valley Forge, Pa.) for dynamic mechanical testing aboard a simulated NIMBUS-B sensory ring.

SNAP-15. Work is in progress to improve and upgrade the SNAP-15 1-mw generator being developed for possible use with control instrumentation. Current efforts are directed toward perfecting an outer canister seal and an improved electrical insulation for the generators. Developed by the General Atomic Division of General Dynamics, SNAP-15A is capable of supplying its rated power under extreme conditions of temperature, shock, and vibration.

SNAP-11. A thermoelectric generator capable of producing between 20 and 25 electrical watts is being prepared by the Martin Co. for loading with a ^{242}Cm radioisotope heat source in mid-1966. Electrically heated prototype models will be delivered to NASA's Jet Propulsion Laboratory (Pasadena, Calif.) and the Manned Spacecraft Center in Texas for environmental and compatibility testing.

SNAP-9A. The two Martin-developed SNAP-9A generators that were launched into orbit in September and December 1963 provided all the power required by two of the Navy's navigational satellites for the life of the functional satellite components. The telemetry data received since launch indicates that, although the stability of power output of the generators was adequate, there were design deficiencies in SNAP-9A (notably in the hermetic seals of the generator housing and in the thermoelectric materials used) which have caused a power degradation rate greater than predicted before launch. These design deficiencies have been taken into account in the designs of newer power systems. SNAP-9A is still operating, although its power output is degraded owing to a leak of helium from the generator and the day–night thermal-cycling effect upon the thermoelectric materials.

Earlier aerodynamic analysis had predicted the burnup of the ^{238}Pu fuel inventory of the SNAP-9A space nuclear generator that failed to achieve orbit in April 1964. These predictions have been verified through analyses, made in 1964 and 1965 by the AEC's Health and Safety Laboratory in New York City, of samples of radioactive material collected in the upper atmosphere by balloons. The analyses of the balloon samples clearly indicate that upon its reentry into the earth's atmosphere, the SNAP-9A's fuel burned up to submicron-size particles at an altitude of more than 130,000 ft, underwent global distribution, and hence presents no health hazard.

SNAP-3. On June 29, 1965, the first nuclear power generator to be launched into space marked its fourth anniversary. During its $4\frac{1}{2}$ years in orbit aboard a 175-lb drum-shaped experimental DOD (Navy) navigational satellite, the 5-lb grapefruit-sized generator, which was developed by the Martin Co., Baltimore, Md., has traveled more than 500 million miles. Although the satellite electronics have ceased to operate, the generator is still producing power at a degraded level.

Radioisotope Production and Separations Technology

Industry is becoming more active in preparing radioisotopes, resulting in the systematic withdrawal of the AEC from this area as private capability develops. Research and development on production–separation technology, however, is planned for FY 1967. When the Fission Products Conversion and Encapsulation Plant goes into operation in calendar year 1968, AEC plans to discontinue production and distribution of the fission products ^{90}Sr, ^{147}Pm, ^{144}Ce, and ^{137}Cs.

SELECTED STUDIES AND EVENTS FOR 1965–1966

Sales. During 1965 a total of more than 1.2 million curies of processed radioisotopes were distributed from ORNL. This represents about a 50% increase in curies* over 1964, mainly owing to increased demands for ^{60}Co, ^{137}Cs, and ^{3}H. An additional noteworthy shipment was 670,766 curies of ^{60}Co from the Savannah River Laboratory (SRL) to Brookhaven National Laboratory (BNL) for use in the High Intensity Radiation Development Laboratory.

Withdrawals and Price Changes. The AEC withdrew from the preparation (for purposes of

*Actual shipments decreased by 24% as a result of the recent transfer of a number of radioisotopes to private industry.

sale) of ^{125}Sb, ^{45}Ca, ^{59}Fe, ^{75}Se, ^{113}Sn, ^{65}Zn, and ^{85}Sr. On May 1, 1966, AEC withdrew from routine production and distribution of 19 other radioisotopes in consideration of a formal petition [see *Isotopes and Radiation Technology*, 3(2): 174 (Winter 1965–1966), and page 292 of this issue]. The AEC reduced the prices on 12 radioisotopes and increased the prices on 52 others during the early part of 1965 [*Isotopes and Radiation Technology*, 2(3): 317-318 (Spring 1965)].

Krypton-85 Enrichment. A thermal-diffusion facility has been installed and tested at ORNL for increasing the isotopic concentration (from 5 to 45%) of the fission-product radioisotope, ^{85}Kr. This higher isotopic concentration will increase the usefulness of ^{85}Kr in commercial applications such as luminous signs and radioisotope density gages. With normal feed material (containing 5% radioactive ^{85}Kr and miscellaneous amounts of stable ^{82}Kr, ^{83}Kr, ^{84}Kr, and ^{86}Kr), an annual output of 3000 curies of 45% ^{85}Kr can be obtained through two thermal-diffusion cascades containing 216 electrically heated tubes.

Technetium-99m Generator. BNL and Argonne Cancer Research Hospital have cooperated in developing methods for preparing and utilizing ^{99m}Tc. This nuclide is formed by the decay of a fission product, 67-hr ^{99}Mo, which can be loaded onto a "generator" from which the metastable ^{99m}Tc (6-hr half-life) is rapidly and easily "milked" [see *Isotopes and Radiation Technology*, 2(1): 91 (Fall 1964)].

Isotopic Power Fuels. Production of ^{238}Pu as a by-product of current production operations continued at Savannah River Plant during the year. New methods to increase production are being considered. Primary efforts are directed toward necessary ^{236}U concentration in the enriched ^{235}U fuel. The ^{236}U is reinserted in the reactor to generate ^{237}Np, which is separated and irradiated as a target element to form ^{238}Pu. Test quantities of fuel forms of ^{238}Pu with melting points above 2000°C were prepared at Mound Laboratory. Facilities for the fabrication and characterization of large sources for use as space power units are being installed with operation scheduled in 1966. Studies will emphasize encapsulation systems for long-term operation at high temperature and burnup upon reentry from space.

The initial irradiation of ^{239}Pu to produce ^{242}Pu was completed in early 1965. Target elements were fabricated at ORNL and SRL for further irradiation under high-flux conditions [10^{15} n/(cm^2)(sec)]. Special facilities for chemical separation of the curium are being provided in the Savannah River Laboratory. Gram quantities of ^{244}Cm have already been obtained as a by-product of another program. At ORNL and SRL, curium work has included the acquisition of chemical- and physical-property data of the compound and source forms along with the development of encapsulation techniques. At ORNL, 10 g of ^{242}Cm, the largest quantity ever processed, was purified. ORNL also has processed about 10 g of ^{244}Cm from SRL feed material. A 2.4-g prototype source of ^{244}Cm has been successfully fabricated; about 5 g are being prepared for critical-mass measurement, and the remainder is being used for properties studies.

A total of 5 million curies of ^{60}Co has been produced and distributed from AEC reactors since 1955. Nearly 16 million curies were being produced or planned for production at the end of 1965. This includes one lot of approximately 1 million curies at specific activities from 300 to 700 curies/g and will be the highest specific activity cobalt ever produced. SRL is developing ^{60}Co isotopic fuels technology for applications requiring up to 400 kw of thermal energy. DOD and NASA are interested in large-scale use of ^{210}Po isotopic fuel for missions up to 90 days. Detailed studies have been made of production reactors for making ^{210}Po in thermal megawatt quantities. At Mound Laboratory, in support of the radioisotopic space-thruster program, a prototype capsule was fabricated and operated at 1450°C for 72 hr. A number of polonium compounds can be used for applications in the temperature range of 1600 to 2000°C, and several compounds are being intensively studied for space applications. The properties of refractory metals and alloys are being examined to find more suitable materials to encapsulate the polonium fuel at these temperatures.

Process Radiation Development

This program has three main aspects: basic technology, radiation engineering, and specific process applications. The FY 1967 budget is divided about equally among these three areas. Effort will be exerted to effect a pilot-plant

demonstration of the radiation manufacture of wood–plastic combinations and of polyethylene. Letters have been sent to industrial firms and others about the types of AEC assistance in the construction and operation of pilot facilities for these processes.

SELECTED STUDIES AND PROCESSES FOR 1965–1966

During 1965 AEC continued sponsorship of research to determine the nature of significant chemical reactions through studies on the two major mechanisms of ionic and free-radical transformations. Measurements of yields of potentially important radiation-induced reactions and the rates at which these reactions proceed are being determined. Research includes: (1) reactions between amines and olefins, (2) oxidation–reduction reactions in doped inorganic laser crystals, (3) emulsion polymerization of vinyl acetate, (4) effects of radiation on colloidal systems, and (5) radiation-induced fluorination of hydrocarbons.

Wood–Plastic Combinations. The AEC's program for developing the process for wood–plastic materials production was significantly expanded during 1965 and 1966. [The developments have been extensively reviewed recently in *Isotopes and Radiation Technology*, 3(2): 115-146 (Winter 1965–1966)].

Radiation-Produced Polyethylene and Copolymers. A process for the continuous production of polyethylene and ethylene copolymers has been under study at BNL. The process seeks to replace conventional proprietary catalysts, such as organic peroxides, with gamma radiation.

Earlier work was performed in small-batch experiments. During 1965 a continuous-flow apparatus was constructed to obtain meaningful information on reaction kinetics. High conversion rates, comparable to commercial rates at conventional high-pressure conditions, have been obtained for ethylene polymerization.

A wide variety of ethylene copolymer plastics have been formed at room temperature, using such monomers as carbon monoxide, sulfur dioxide, styrene, methyl methacrylate, vinyl acetate, acrylonitrile, allyl acetate, isobutylene, chlorotrifluoroethylene, *trans*-2-butene, methyl acrylate, isoprene, propylene, vinyl chloride, 1-butene, *cis*-2-butene, vinyl pyrrolidone, methyl vinyl ketone, and divinyl benzene. These have all been produced at room temperature. For the case of the ethylene–carbon monoxide copolymers, products of high molecular weight with high melting points have been formed at 68°F. A crystalline melting point of 465.8°F and an onset of decomposition at 482°F were measured for a 50% carbon monoxide copolymer.

Radiation Preservation of Foods

Increasing efforts in FY 1967 are planned for obtaining clearances of selected foods from the Food and Drug Administration (FDA) and for commercialization. These are essentially the recommendations of an advisory committee from the American Institute of Biological Sciences and of the AEC's Advisory Committee on Isotopes and Radiation Development.

A detailed analysis on the relative costs and benefits of radiation processing of selected foods will be concluded early in FY 1967. A petition for clearance of strawberries is in preparation, and other petitions for clearance of two radiation-processed fishery products, five fruits, and frozen chicken will be submitted to FDA in FY 1967.

Several food irradiators presently are being designed or built. Final construction plans are being drawn for the Hawaiian Development Irradiator. The state of Hawaii is investing approximately $200,000 in the building that will house the facility, and the state Department of Agriculture has been authorized to plan commercialization ventures with the Hawaiian fruit industry. AEC provided $350,000 toward this project[5a] in FY 1966. The AEC and DOD are planning another cooperative program with industry for the construction and operation of a demonstration meat irradiator [see *Isotopes and Radiation Technology*, 3(2): 168-169 (Winter 1965–1966) .

SELECTED DEVELOPMENTS FOR 1965–1966

The JCAE hearings on food irradiation in June 1965 will be covered in *Isotopes and Radiation Technology*, 3(4).

Status of Research and Development. Radiation preservation of the five species of seafoods continued to show promise for ultimate commercialization, and other seafoods (such as sole, ocean perch, pollock, and cod) have been added to the program. Some of the fruits (such

as lemons and grapes) selected initially, however, have failed to respond well to radiation treatment and have been replaced by more promising candidates (such as bananas, papayas, and mangoes). Approximately 13 varieties of seafood and 15 varieties of fruits, vegetables, and grains are now under intensive study. No new FDA approvals of food were made during 1965. A petition was accepted for consideration by the FDA on Sept. 8, 1965, which involves the clearance of six species of fish (cod, flounder, haddock, ocean perch, pollock, and sole), in connection with work supported at the Bureau of Commercial Fisheries.

International activity in this field is beginning to gather momentum, and the AEC is providing support in the form of personnel and a large ^{60}Co source to the International Center for Food Irradiation at Seibersdorf, Austria, where a program on radiation pasteurization of fruit juices is receiving major consideration.

Demonstration Programs. An AEC solicitation to industry in May 1965 for participation in the food-irradiation program met with an enthusiastic response. Some 20 commercial-fish-processing companies are now using the Marine Products Development Irradiator at Gloucester, Mass., for large-scale testing of several marine products under cooperative arrangement with the AEC and the Bureau of Commercial Fisheries. None of the companies were using the facility prior to May. A solicitation of interest of firms in a meat radiation-sterilization facility was made on Sept. 24, 1965, proposing construction of a facility with private funds. More than 40 meat packers and construction companies showed an interest in such a project.

Irradiators. During 1965 the truck-mounted Mobile Gamma Irradiator (MGI) was completed by the Vitro Engineering Co. and sent to California for final checkout and field operation by the University of California. The mobile unit will be used for large-scale processing of fruit, including strawberries, bananas, and peaches, during the 1966 crop season.

The Grain Products Irradiator (GPI) located in Savannah, Ga., was under construction by the Vitro Engineering Co. Although originally intended for insect disinfestation in grains, the GPI has drawn interest from processors of packaged mixes, cereals, and flours who have expressed a desire to cooperate in test irradiations of their products. The design of the irradiator has been modified to accommodate these uses.

Two shipboard irradiators were fabricated for the AEC by Nuclear Materials & Equipment Corp., Apollo, Pa. The first is to be on a U. S. Department of Interior fishing vessel working out of Gloucester, Mass. The second unit will operate in 1966 out of Pascagoula, Miss. A third such unit was ordered from Radiation Facilities, Inc., Lodi, N. J., and will be used cooperatively with selected firms in the poultry- and fruit-processing industries.

JCAE Questions and AEC Answers

Comments by the JCAE after Fowler's testimony were largely directed toward food irradiation and industry participation. The following summary is based on a recent report[6] of the hearings discussion.

DEMONSTRATION PROGRAMS

Rep. Craig Hosmer (R.-Calif.) asked about the extent of AEC assistance in demonstrating processes to industry. AEC Commissioner James T. Ramey said that AEC would provide the radiation source and some assistance in design. JCAE Executive Director John T. Conway reported that AEC participation in demonstration projects involved $110,000 for wood plastics and a 60% maximum in polyethylene. Fowler commented that AEC intends to develop maximum private investment in demonstration programs.

RATE OF COMMERCIALIZATION

Several comments dealt with "getting the show on the road" in food irradiation. Fowler denied that industry hesitancy to accept the process stems from inability to monopolize (or patent) applications, active opposition from proponents of other types of processes, or objections by particular agricultural food areas.

Ramey noted that AEC tries to spread facilities geographically.

Rep. Chet Holifield (D.-Calif.) asked whether or not the *fear* of an adverse psychological reaction of people to irradiated food might result in a lack of enthusiasm by the meat industry. Fowler replied that the lack of a sufficient number of FDA-cleared foods was a more potent deterrent to commercialization.

EXTENT OF INDUSTRY PARTICIPATION

Fowler repeatedly asserted that industry was not participating to a great extent because FDA has not cleared sufficient irradiated foods to constitute a reasonable food business.

Holifield asked if AEC decided not to go ahead on a food-irradiation pilot plant. Ramey and Fowler said AEC wanted to get greater industrial participation before asking congressional authorization for this project.

Fowler, in replying to a question by Hosmer about the type of interest shown by industry in the pilot-plant meat irradiator, said (1) industry generally looked at food irradiation as a high-risk venture and (2) AEC's feeling was that the government should go out for a joint project and have proposals come in from industry for investment of $1 million.

Questioning later turned to the bids sought by the U. S. Army for 30,000 lb of irradiated bacon in early 1965 and the Army's receiving two responses. DID's Justin L. Bloom noted that the Army had been careful to reword the request, which was difficult to understand, and was also working with AEC to develop a radiation facilities list. He also pointed out that no commercial facilities are available in the United States to provide the irradiated bacon and that an AEC irradiator might be used.

Rep. Thomas G. Morris (D.-N. Mex.) requested that DID submit for the record a list of all proposals or expressions of interest in a DID project by industry.

ISOTOPIC HEAT SOURCES

Holifield pointed out that some people have claimed that AEC is not actively pursuing the market for isotopic heat sources or satisfying the customers in the present market. He asked if AEC is capable of supplying them and whether or not this activity should be allocated. Fowler replied that (1) AEC has the only capability at this time and is meeting the needs for new types of sources as fast as technology can be developed and (2) industry fabrication should occur later.

Rep. John B. Anderson (R.-Ill.) said he felt that last year NASA was not interested in these sources. Ramey, stating that NASA has shown increased interest, noted a reorganization to put "space isotopes" under Harold Finger.

(D. A. Fuccillo Jr.)

AEC Withdraws 19 Radioisotopes, Recieves Comments on Services

AEC withdrew 19 radioisotopes from routine production and distribution on May 1, 1966. This recent action brought to a total of 33 the radioisotopes* that AEC has discontinued producing routinely [*Isotopes and Radiation Technology*, 2(3): 317 (Spring 1965)].

The withdrawal is in accordance with AEC's formal policy, adopted in March 1965, for transfer of routine production and distribution to industry as rapidly as possible consistent with the national interest. AEC continues to supply purchasers who state in writing that the material they need is of a technical quality not commercially available.

AEC gave notice of intent to withdraw both through releases and in the *Federal Register* on Jan. 25–26, Mar. 31, and Apr. 2, 1966. The 17 written comments received were not considered by AEC of such substance as to require changes in the proposed withdrawal. AEC announced that private organizations are producing these isotopes in sufficient quantity to meet ordinary commercial demands and at reasonable prices.

Some of the comments have been published in *Atomic Energy Clearinghouse*, 12(8): 16-17; 12(9): 16; 12(10): 9-10; 12(11): 22 (1966): all are on file at the AEC Public Document Room, located at 1717 H Street, N. W., Washington, D. C. Three of the published comments indicate approval of AEC action in withdrawing the 19 radioisotopes. Of the other seven, two were concerned with a single isotope—^{42}K. Concern was expressed about obtaining high-specific-activity material on a regular basis from commercial suppliers. Copper-64 withdrawal also was opposed; a research biochemist stated that he could only find one commercial supplier of this radioisotope and that he required higher specific activity than the supplier advertised. Additional comments referred to isotopes for teaching purposes (reasonable cost stressed), the need for adequate controls and a clearinghouse for availability information, and apparent inadequacy of some commercial services.

*The 33 radioisotopes are as follows: ^{110m}Ag, ^{76}As, ^{77}As, ^{198}Au, ^{199}Au, ^{82}Br, ^{45}Ca, ^{109}Cd, ^{115}Cd, ^{115m}Cd, ^{141}Ce, ^{58}Co, ^{51}Cr, ^{134}Cs, ^{64}Cu, ^{55}Fe, ^{59}Fe, ^{197}Hg, ^{203}Hg, ^{42}K, ^{125}I, ^{131}I, ^{140}La, ^{99}Mo, ^{24}Na, ^{32}P, ^{35}S(sulfate), ^{124}Sb, ^{125}Sb, ^{75}Se, ^{113}Sn, ^{85}Sr, and ^{65}Zn. In addition, AEC supplies ^{60}Co and ^{192}Ir in metallic sources under special conditions.

AEC Changes Prices of 13 Radioisotopes

AEC increased prices of 13 radioisotopes on May 1, 1966. The price increases were necessary to recover full costs of radioisotope production and distribution.

The radioisotopes are: ^{60}Co solution, ^{152}Eu, ^{181}Hf, ^{114}In, ^{194}Ir, ^{55,59}Fe, ^{191}Os, ^{86}Rb, ^{46}Sc, ^{182}Ta, ^{185}W, ^{90}Y, and ^{3}H (targets).

Copies of the revised price schedule may be obtained from J. E. Ratledge, Oak Ridge National Laboratory, Isotopes Sales Department, Isotopes Development Center, P. O. Box X, Oak Ridge, Tenn. 37830.

AEC Motion Pictures Available

The AEC has made available for loan and sale 16 technical motion pictures from AEC's domestic and overseas film libraries. The 16-mm color films range in length from 5½ to 40 min, and they are listed below:

ACCEL: Automated Circuit Card Etching Layout, 20 min, produced for AEC by the Sandia Corporation

Acromegaly: Diagnosis-Etiology-Therapy, 23 min, produced by Donner Laboratory and the AEC's Lawrence Radiation Laboratory

Clean Air Is a Breeze, 16 min, produced for the AEC by the Sandia Corporation

Current Methods in Plutonium Fuel Fabrication, 30 min, produced by AEC's Hanford Atomic Products Operation

Fabrication of the Accelerator Structure, 40 min, produced by AEC's Stanford Linear Accelerator Center

Neutron Image Detector, 5½ min, produced by AEC's Argonne National Laboratory

Pax Atomis: SNAP-7 Terrestrial Isotopic Power Systems, 25 min, produced for the AEC by the Martin Co.

RFD-2, 14 min, produced for the AEC by the Sandia Corporation

SNAPTRAN 2/10A Water Immersion Test, 20 min, produced for the AEC by the Phillips Petroleum Company

SPERT Destructive Test Part I (on Aluminum Highly Enriched Plate Type Core), 15 min, produced for the AEC by the Phillips Petroleum Company

A Study of Grain Growth in BeO Using a New Transmitted Light Hot Stage, 16½ min, produced for the AEC by Atomics International

Ternary Phase Diagram, 7 min, produced by the AEC's Lawrence Radiation Laboratory

The Nuclear Witness: Activation Analysis in Crime Investigation, 28 min, by General Atomic Division of General Dynamics Corp.

Transcurium Elements: Synthesis, Separation and Research, 31 min, by the AEC's Lawrence Radiation Laboratory

Transportation of Radioactive Materials, Part II, Accidents, 34½ min, produced by the AEC's Division of Operational Safety

The Wooden Overcoat, 14 min, produced for the AEC by the Sandia Corporation

AEC Plans To Develop Cardiac Pacemaker as Self-Contained Nuclear-Powered Unit

AEC has initiated a program to develop a self-contained radioisotope-powered cardiac pacemaker to be used for treatment of "heart block," a common cardiac disease.

The pacemaker is not a mechanical heart; it is a heartbeat stimulator. Current pacemakers are battery powered. The nuclear device would be developed for eventual insertion in the body by surgery.

AEC has invited technical proposals for research and development. The decision to initiate this program was based on extensive technical discussions between the AEC and the medical community. These discussions, together with preliminary engineering studies, have led to the conclusion that the development of a nuclear-powered pacemaker is technically feasible. The National Heart Institute of the National Institutes of Health, Bethesda, Md., and the Newark Beth Israel Hospital, Newark, N. J., both of which participated extensively in the discussions, will assist the AEC in the technical evaluation of the program.

The primary objective of this program is the development of a nuclear-powered pacemaker with a minimum operating lifetime of 10 years. This lifetime is two to three times that of existing battery-powered commercial pacemakers. As a result, its use would significantly reduce the number of surgical operations required to replace a shorter-lived device. The nuclear-powered pacemaker is expected to operate at a very low power level of several hundred microwatts and would be fueled with ^{238}Pu.

Other important objectives that have been established are: the reduction of radiation exposure to the body to medically acceptable levels, absolute containment of the radioisotope fuel, and reduction of the size and weight of the pacemaker sufficient to accomplish surgical implantation. To achieve the specified operating lifetime and at the same time minimize size, weight, and radiation characteristics, ^{238}Pu has been selected as the radioisotope fuel, primarily because of its low shielding requirements and also because of its relatively long half-life (89.6 years).

The initial phase of this program will consist in engineering design, component develop-

ment, and short-term testing of experimental models. The total estimated cost of this first phase is $500,000 to $750,000. This phase is expected to be completed within 12 to 24 months. A second phase would include assembly and fabrication of fueled prototype units and extensive performance, endurance, and environment testing (including testing in animals) necessary to demonstrate the attainment of program objectives.

General

Revised Half-Lives

The Isotopes Development Center of ORNL is continually evaluating half-life values for those isotopes now or formerly routinely available from the Laboratory. Compilations by the ORNL Nuclear Data Group are extremely valuable in such evaluations. Table VIII-4 compares old values with the new "best" values now suggested for a number of these isotopes.

Table VIII-4 COMPARISON OF OLD AND NEW HALF-LIFE VALUES

Isotope	$T_{\frac{1}{2}}$ (new)	$T_{\frac{1}{2}}$ (old)
^{125}Sb	2.7 years	2.78 years
^{14}C	5.73×10^3 years	5.57×10^3 years
^{60}Co	5.26 years	5.24 years
^{3}H	12.3 years	12.46 years
^{125}I	60 days	57.4 days
^{55}Fe	2.7 years	2.94 years
^{59}Fe	45 days	44.3 days
^{85}Kr	10.6 years	10.27 years
^{197}Hg	64 hr	65 hr
^{203}Hg	46.5 days	45.4 days
^{63}Ni	92 years	125 years
^{147}Pm	2.65 years	2.5 years
^{35}S	88 days	89.0 days
^{204}Tl	3.8 years	3.57 years
^{113}Sn	118 days	119 days
^{185}W	74 days	75.8 days
^{65}Zn	245 days	246.4 days

Quebec Firm Ships "Sproutless" Potatoes from Multipurpose Irradiator

Newfield Products, Ltd., in March 1966 shipped 50,000 lb of irradiated potatoes to a Toronto distributor, the first such shipment of its kind. The potatoes were processed at Newfield's $1.2 million plant near Montreal, Quebec, Canada.

According to *Nuclear Industry*[7] the potatoes will be sold over the counter to Canadian customers. They are labeled "sprout inhibited by gamma energy." Newfield plans to sell 5 million lb by midsummer 1966. Wholesale prices are a few cents per 100 lb higher than those of potatoes treated with chemicals to inhibit sprouting.

The irradiation of potatoes will occupy the facility for approximately 10% of the available irradiation time. In addition to contract irradiations, Newfield is investigating commercial irradiation of other foods.

A brief description of the Newfield irradiator, extracted from an article by Popoff,[8] follows:

> Two major investor groups—Canadian Enterprise Development Corp. of Montreal and Research and Science Investors of New York—backed the enterprise. The company is under Canadian control and is spending approximately $1.3 million during its initial phase of operation.
>
> The plant consists of a ^{60}Co gamma irradiator, a laboratory, and a 15-million-lb potato-storage warehouse. The irradiation facility was designed, built and installed by Commercial Products Division, Atomic Energy of Canada Ltd.
>
> The irradiation chamber is 21 by 36 ft and 16 ft high. Biological shielding is provided by 5-ft-thick walls of standard density concrete which reduce radiation fields to 0.25 mrh or less on the outside when a 600,000-curie source is in operation. The product is conveyed to the source through a protective labyrinth on a chain-driven conveyor.
>
> In operation, pallet boxes are automatically transported into and out of the irradiation chamber.
>
> The initial ^{60}Co source is 34,000 curies and is made up of 1 in. dia by 18 in. pencils attached to a flexible rack resembling a rope ladder. When the source is raised into the irradiation chamber, it takes an annular configuration (center cavity, 17 in. in dia by 36 in. long) within the source guard which protects it from mechanical damage and dirt from pallet boxes.
>
> The irradiator can process any material which can be fitted into the transport pallet boxes (48 in. × 42 in. × 40 in.). Dose rate inside the source cavity is approximately 2×10^5 rads/hr.
>
> When the irradiator is not in use, the source rack is lowered to the bottom of an 18-ft-deep, water-filled pool.

New Publication, Isotopenpraxis, Started

A new publication in the field of isotope technology, *Isotopenpraxis*, was started in October 1965 by the Akademie-Verlag, which also publishes *Kernenergie*. The new publication is similar in format to the older one and is printed in German with German, English, and Russian abstracts. The first two issues ran to 92 pages

total and included articles on uses of stable isotopes, autoradiography of doubly labeled materials, thickness and moisture gages, neutron–gamma probes, leak detection with ^{85}Kr, labeled drugs, and quantitative analysis by beta-backscattering techniques. Book reviews, conference news, and short subjects are also presented.

The address of the publisher is Akademie-Verlag GmbH, Redaktion *Isotopenpraxis*, Leipziger Strasse 3-4, Berlin 108.

NBS Institute for Materials Research Sets Symposium on "Trace Characterization"

An international symposium on Trace Characterization — Chemical and Physical, sponsored by the National Bureau of Standards (NBS) Institute for Materials Research, will be held Oct. 3–7, 1966, at NBS, Gaithersburg, Md.

The program deals with the following general areas of trace characterization:

1. Electrical (e.g., resistivity, Hall effect, dielectric relaxation)
2. Spectroscopic (e.g., emission, X-ray, including microprobe, atomic absorption)
3. X-ray diffraction (e.g., lattice parameter, electron density, topography)
4. Optical (e.g., color center studies, light scattering, spectrophotometry)
5. Electrochemical (e.g., polarography)
6. Nuclear (e.g., activation analysis, radioisotope dilution)
7. Resonance (e.g., electron spin resonance, nuclear magnetic resonance)
8. Mass spectroscopy (e.g., spark source, isotope dilution)
9. Electron and optical microscopy (e.g., replica and transmission techniques, electron diffraction)
10. Sample preparation, preconcentration, handling, reagents, etc.

Announcements concerning this symposium are available from: Roger G. Bates, Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234.

Both invited lectures and selected contributed papers will be published in a volume to be prepared from the proceedings of the symposium. General chairman of the symposium is W. Wayne Meinke. Bourdon F. Scribner is technical program chairman.

References

1. *Major Activities in the Atomic Energy Programs, January–December 1965*, U. S. Government Printing Office, Washington, January 1966.
2. E. E. Fowler, Statement at the FY 1967 Authorization Hearings Before the Joint Committee or Atomic Energy, Mar. 8, 1966, in press.
3. *U. S. Atomic Energy Commission 1965 Financial Report*, Office of the Controller, U. S. Government Printing Office.
4. Isotopes and Radiation, *Nucl. News*, 9(3): 1' (March 1966); see also p. 13.
5. *At. Energy Clearinghouse*, 12(4), Suppl. 15: 1 (1966).
   a. O. M. Bizzell, Division of Isotopes Develop ment, AEC, personal communication, May 2(1966.
6. *At. Energy Clearinghouse*, 12(11): 32-34 (1966).
7. *Nucl. Ind.*, 13(3): 21-22 (March 1966).
8. D. Popoff, Quebec Gets World's First Food I: radiator, *Can. Nucl. Technol.*, 4(3): 20-25 (Sun mer 1965).

LEGAL NOTICE

This journal was prepared under the sponsorship of the U. S. Atomic Energy Commission. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this journal, or that the use of any information, apparatus, method, or process disclosed in this journal may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this journal.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

☆ U. S. GOVERNMENT PRINTING OFFICE: 1966—202-798/3

NUCLEAR SCIENCE ABSTRACTS

The U. S. Atomic Energy Commission, Division of Technical Information, publishes *Nuclear Science Abstracts* (*NSA*), a semimonthly journal containing abstracts of the literature of nuclear science and engineering.

NSA covers (1) research reports of the U. S. Atomic Energy Commission and its contractors; (2) research reports of government agencies, universities, and industrial research organizations on a worldwide basis; and (3) translations, patents, books, and articles appearing in technical and scientific journals.

Complete indexes covering subject, author, source, and report number are included in each issue. These are cumulated quarterly, semiannually, and annually providing a detailed and convenient key to the literature.

Availability of *NSA*

SALE *NSA* is available on subscription from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402, at $30.00 per year for the semimonthly abstract issues and $22.00 per year for the four cumulated-index issues. Subscriptions are postpaid within the United States, Canada, Mexico, and all Central and South American countries, except Argentina, Brazil, British and French Guiana, Surinam, and British Honduras. Subscribers in these Central and South American countries, and in all other countries throughout the world, should remit $37.00 per year for subscriptions to semimonthly abstract issues and $25.00 per year for the four cumulated-index issues.

EXCHANGE *NSA* is also available on an exchange basis to universities, research institutions, industrial firms, and publishers of scientific information. Inquiries should be directed to the Division of Technical Information Extension, U. S. Atomic Energy Commission, P. O. Box 62, Oak Ridge, Tennessee, 37830.

TECHNICAL PROGRESS REVIEWS may be purchased from Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402. *Nuclear Safety* at $3.00 per year for each subscription or $1.00 per issue; the other four journals at $2.50 per year or $0.70 per issue. The use of the coupon below will facilitate the handling of your order.

POSTAGE AND REMITTANCE: Postpaid within the United States, Canada, Mexico, and all Central and South American countries except Argentina, Brazil, Guyana, French Guiana, Surinam, and British Honduras.. For these Central and South American countries and all other countries, add $0.75 for each annual subscription or $0.20 for a single issue. Payment should be by check, money order, or document coupons, and MUST accompany order. Remittances from foreign countries should be made by international money order or draft on an American bank payable to the Superintendent of Documents or by UNESCO book coupons.

order form

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON, D. C., 20402

Enclosed:
document coupons ☐ check ☐ money order ☐

Charge to Superintendent of Documents No. _____

Please send a one-year subscription to

☐ ISOTOPES AND RADIATION TECHNOLOGY

☐ POWER REACTOR TECHNOLOGY

☐ REACTOR FUEL PROCESSING

☐ REACTOR MATERIALS

(Each subscription $2.50 per year; $0.70 per issue.)

☐ NUCLEAR SAFETY

(Each subscription $3.00 per year; $1.00 per issue.)

SUPERINTENDENT OF DOCUMENTS
U. S. GOVERNMENT PRINTING OFFICE
WASHINGTON, D. C., 20402

(Print clearly)

_____
Name

_____
Street

_____
City, State, ZIP Code